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PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. X] *SECTION A* [NO. 6

DECEMBER, 1939

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, HEBBAL, BANGALORE.

STUDIES IN THE CHEMICAL BEHAVIOUR OF SULPHUR COMPOUNDS

Part I. The Hydrolysis of Sulphur Chloride

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Received November 2, 1939

It is well known that the hydrolysis of sulphur chloride is a very complicated reaction, yielding sulphur and a number of sulphur compounds. The nature of the primary product has all along been a matter of controversy, because of its great reactivity and the consequent formation of various secondary products.

As far back as 1845, Plessy[32] pointed out that sulphur chloride, when brought in contact with water, undergoes hydrolysis, yielding hydrochloric acid, elementary sulphur and several oxyacids of sulphur. Fordos and Gelis[12] suggested that pentathionic acid was the polythionic acid primarily formed. Debus[7] attributed the formation of thiosulphuric acid as a product of the reaction, to the combination between nascent sulphur and sulphurous acid. Noack[29] showed that the products of hydrolysis were the same as those obtained by the reaction between hydrogen sulphide and sulphur dioxide in forming Wackenroder's solution. He suggested that the first stage of hydrolysis yielded thiosulphurous acid ($H_2S_2O_2$) which on decomposition would produce hydrogen sulphide and sulphur dioxide. Attempts by Noack to prepare thiosulphurous acid by the interaction between the two gases, in absence of water, failed. Neumann and Fuchs[28] pointed out that the hydrolysis was incomplete, as only 94% of the chloride reacted with water. The yield of sulphur was 65% and of the polythionic acids 32%, the principal acid being pentathionic acid (18%).

Olin[30] considered hydrogen sulphide and sulphur dioxide to be the primary products and assigned to sulphur chloride the structure S : S (: Cl_2).

In all these investigations, as high concentrations of sulphur chloride had been used, the concentration of the primary product of hydrolysis was high and owing to its great chemical activity, a number of secondary reactions took place, yielding a variety of sulphur compounds. Furthermore, owing to the acidity developed during hydrolysis of the chloride, the secondary effects were rendered highly complex and a quantitative interpretation of the phenomenon was impossible.

In the investigations described in the present paper, the reaction has been elucidated by a new technique, the hydrolysis being carried out at the interface between very dilute solutions of sulphur chloride in carbon tetrachloride and aqueous alkali in presence of cadmium hydroxide. The alkali and the cadmium hydroxide circumscribed the scope of secondary reactions and rendered possible a quantitative interpretation of the phenomenon.

Experimental

Carbon Tetrachloride.—"Chemically pure" carbon tetrachloride was shaken with mercury to remove traces of sulphur. It was then dried over phosphorus pentoxide and distilled in an all-glass apparatus provided with a spray trap. The distillate was tested with mercury and found to be absolutely free from sulphur.

Sulphur Chloride.—A supply of C.P. quality from the British Drug House was mixed with 1% its weight of each of active charcoal and pure sulphur and heated at the temperature of the water bath for a period of four hours in an all-glass apparatus consisting of a flask, a reflux condenser and a device for the exclusion of atmospheric moisture. The chloride was then distilled under reduced pressure (28 mm.) at about 42° C. using a suitable all-glass apparatus (Harvey and Schuette[17], Lowry, McHatton, and Jones[24]). The middle fraction of the distillate was immediately diluted with purified carbon tetrachloride and stored in the dark in an apparatus in which the chloride was carefully protected from atmospheric moisture and from which portions of the solution could conveniently be withdrawn without exposure to atmospheric moisture. The sulphur chloride in the solution suffered no decomposition even after prolonged storage as could be gathered by periodical analysis.

Analysis of the Sulphur Chloride.—To analyse sulphur chloride, Kretov[20] digested a known weight of the chloride with 2 N alkali on the water bath and oxidised the products of hydrolysis with hydrogen peroxide to obtain the alkali chloride and sulphate. The chloride was determined by Volhard's method and the sulphate gravimetrically as barium sulphate. It was found in this laboratory (both by the author and by Mr. M. R. A. Rao) that while this method gave satisfactory values for chloride, the sulphur values were rather low owing to incomplete oxidation of elementary sulphur produced during hydrolysis. The sulphur could be estimated much more accurately by the following method developed in this laboratory (B. S. Rao and M. R. A. Rao[34]). A known weight of the sulphur chloride solution was shaken up with pure mercury and the mercuric sulphide formed was treated in a suitable all-glass apparatus with a mixture of potassium iodide and

concentrated hydrochloric acid to which a small quantity of hypophosphorous acid had been added. A current of hydrogen was passed through the solution and the hydrogen sulphide liberated was quantitatively absorbed by a zinc hydroxide suspension in dilute alkali. The zinc sulphide was estimated iodometrically when macro quantities were present and colorimetrically (using the methylene blue reaction) when the quantity was small. The analytical results obtained with all the samples of sulphur chloride used in this investigation showed that in them the ratio of S to Cl was exactly unity. The author found no experimental evidence which could confirm the opinion of Terrey and Spong[45] that sulphur chloride purified by distillaton with active charcoal had always a slight excess of sulphur.

Investigations carried out in this laboratory by M. R. A. Rao showed that sulphur chloride could very accurately be estimated by treatment with finely powdered and dried potassium iodide. The possibility of the iodometric estimation of sulphur chloride had been indicated by Spong.[42] His method, however, yielded results of only moderate accuracy. The method developed by M. R. A. Rao was the following :

A known weight (8 g.) of an approximately 0·05 molar solution of the chloride in carbon tetrachloride was transferred to a stoppered bottle, which had been carefully dried previously and which contained 25 c.c. carbon tetrachloride and potassium iodide crystals dried in a vacuum desiccator over phosphorus pentoxide. The bottle was shaken for 10 minutes. Sulphur iodide was liberated and this decomposed completely on keeping for a few hours. After six hours, the liberated iodine was titrated with standard thiosulphate.

The results of a typical analysis of the stock solution of sulphur chloride are given below :

By Kretov's method of analysis it was found that 1 g. of the solution had Cl corresponding to $9{\cdot}605 \times 10^{-5}$ g. atoms. The S as determined by the method of B. S. Rao and M. R. A. Rao was found to be $9{\cdot}560 \times 10^{-5}$ g. atoms. Estimated by the method of M. R. A. Rao the sulphur chloride was found to correspond to $9{\cdot}606 \times 10^{-5}$ g. atom of sulphur per g. of stock solution.

Hydrolysis of Sulphur Chloride.—A weighed quantity (about 18 g.) of the stock solution of the sulphur chloride was added to a known weight of dry carbon tetrachloride kept in a separating funnel. The requisite volume of an aqueous solution of sodium hydroxide was then added. To the alkali solution had been added previously 2 c.c. of a normal solution of pure cadmium chloride to furnish cadmium hydroxide for the removal of sulphide

produced by hydrolysis. (Kurtenacker and Goldbach[21] employed cadmium carbonate for the removal of sulphide from aqueous solutions. In the present investigation it was found advantageous to use the more rapidly acting cadmium hydroxide.) The separating funnel was attached to a shaking machine and the contents shaken for 10 minutes. On standing for a while, the liquid in the funnel separated into two layers. The carbon tetrachloride layer was tapped off, a small quantity of the solvent was then added to the funnel and after shaking, a further separation effected. The total amount of dissolved sulphur present in the carbon tetrachloride layer was determined by employing an aliquot for analysis by the method already indicated (B. S. Rao and M. R. A. Rao[34]).

The cadmium sulphide along with the residual cadmium hydroxide was filtered and washed. The sulphide was then estimated iodometrically the precipitate being treated with 0·1 N iodine in presence of acetic acid and the excess of iodine estimated with standard thiosulphate. It was found desirable to add a small quantity of dilute hydrochloric acid, to complete the dissolution of the sulphide, prior to the estimation of residual iodine. The filtrate left after the removal of the cadmium sulphide was diluted to 250 c.c. in a measuring flask and aliquots employed for the estimation of sulphite and thiosulphate by the method of Kurtenacker and Goldbach.[21] Another aliquot was oxidised with hydrogen peroxide in alkaline medium in a platinum dish and the sulphate estimated by the microanalytical method of Pregl. From this sulphate value, after deducting sulphur corresponding to sulphite and thiosulphate, one could determine sulphur originally present in solution as thionate and sulphate. Independent experiments based on the method suggested by Kurtenacker and Goldbach[21] for the determination of sulphate in a solution containing a mixture of the oxyacids of sulphur, showed that measurable amounts of sulphate were produced in a few experiments. Trithionate was also found, usually associated with sulphate, in some cases. The quantities, however, were small.

Results

Under the experimental conditions described above, hydrolysis of sulphur chloride by alkali yielded free sulphur, and the sulphide, sulphite and thiosulphate of sodium (the sulphide reacting with cadmium hydroxide to give cadmium sulphide). Trithionate and sulphate formation (which is considered in the discussion) was noticed in experiments in which dilute alkali had been used for hydrolysis. The trithionate was due to the decomposition of thiosulphuric acid in the following way:

$$2\,H_2S_2O_3 = H_2S + H_2S_3O_6$$

and therefore, in such cases the sulphide and the thiosulphate values were corrected on the following basis: Let a be the number of S atoms present as trithionate, b the observed sulphide and c the observed thiosulphate, in terms of sulphur atoms. Then corrected sulphide $= b - a/3$, and corrected thiosulphate $= c + 4a/3$. A similar correction was applied for sulphate formation on the basis of the reaction:

$$H_2S_2O_3 + H_2O = H_2S + H_2SO_4.$$

The free sulphur liberated in the reaction was mostly present in carbon tetrachloride solution and could be estimated by the method already indicated. When dilute alkali however, was used for hydrolysis a part of the sulphur was liberated in the "amorphous" condition as $S\mu$, in aqueous suspension along with the hydroxide and the sulphide of cadmium and could not conveniently be determined with any great accuracy. Such sulphur was therefore calculated by difference, in the majority of cases, the sulphur corresponding to sulphur chloride and to each of the products of hydrolysis being known.

It was found that the results could best be interpreted quantitatively on the basis that disulphur oxide (if not its highly unstable hydrate—the hypothetical thiosulphurous acid) is the primary product of hydrolysis. A solution of disulphur oxide (in carbon tetrachloride) has actually been obtained in this laboratory for the first time (B. S. Rao[33]) and a paper on its preparation and properties will form Part II of the present studies.

Disulphur oxide has been found to undergo three simultaneous reactions when brought in contact with alkali. The major part of the oxide produces the sulphide and sulphite of sodium in equimolecular proportions and in presence of sodium hydroxide (B. S. Rao[33]):

$$S_2O + H_2O \rightarrow H_2S + SO_2 \text{ Reaction H (Hydrolysis)}$$
$$S_2O + 4\,NaOH = Na_2S + Na_2SO_3 + 2\,H_2O.$$

Part of the sulphite produced above, reacts with disulphur oxide to give sodium thiosulphate:

$$2\,Na_2SO_3 + 2\,S_2O + 2\,NaOH = 3\,Na_2S_2O_3 + H_2O \text{ Reaction T.}$$
(Thionization)

At the same time, the disulphur oxide, in virtue of its instability, decomposes into sulphur and sulphur dioxide:

$$2\,S_2O = 3\,S + SO_2 \text{ Reaction D (Decomposition)}$$

the sulphur dioxide liberated being absorbed by the alkali to give sodium sulphite.

If S_2O corresponding to h atoms of sulphur participates in reaction H, t atoms in reaction T, and d atoms in reaction D, the total quantity of

disulphur oxide produced by the reaction between sulphur chloride and alkali will be $h + t + d$, while $h = 2$ sulphide, $t = 2/3$ thiosulphate, and $d = 4/3$ free sulphur, all quantities being expressed in gram atoms of sulphur. The values of h, t and d can therefore be calculated from the analytical data.

The following relationship between the products of reaction can easily be deduced :

Free Sulphur = Thiosulphate + 3 (Sulphite − Sulphide) for, the free sulphur $= 3d/4$ while thiosulphate $= 3t/2$, sulphite $= h/2 - t/2 + d/4$, and sulphide $= h/2$. Elementary sulphur could thus be determined directly and the quantity obtained compared with the value calculated on the basis of the above relationship. Close agreement between the two values cannot however be expected since the solutions were very dilute and there were inherent experimental errors in some of the determinations. These experimental errors are discussed in a later part of the paper.

In the first series of experiments (Table I) the effect of dilution of the sulphur chloride on the three parallel reactions was studied. The chief

TABLE I

Effect of Dilution of Sulphur Chloride on Hydrolysis by 2N Alkali

No. of experiment	1	2	3	4	5	6	7
* S_2Cl_2 ..	12·0	12·0	12·0	12·0	12·0	8·98	8·98
† Dilution ..	0·7	0·7	1·5	1·5	3·8	38·7	77·1
* Sulphide ..	3·25	3·23	4·11	4·10	4·55	3·98	4·06
* Thiosulphate ..	1·13	1·06	1·11	1·44	1·72	1·10	1·31
* Sulphite ..	4·11	4·20	4·74	4·55	4·56	3·68	3·61
* Sulphur (found)	3·64	3·82	2·55	2·38	1·43	0·21	..
* ,, (calculated)	3·71	3·97	3·00	2·79	1·75	0·20	..
% Hydrolysis ..	54·2	53·8	68·5	68·3	75·8	88·6	90·4
% Thionization ..	6·2	5·9	6·2	8·0	9·6	8·1	9·7
% Decomposition	40·4	42·4	28·3	26·4	15·9	3·1	0·0
TOTAL ..	100·8	102·1	103·0	102·7	101·3	99·8	100·1

* In Table I, the quantities of sulphur chloride and of each of the products of reaction are expressed in gram atoms of sulphur and have been multiplied by 5×10^3.

† In Table I, the dilution of sulphur chloride is expresssed in grams of solvent per gram atom of sulphur as sulphur chloride and has been multiplied by 10^{-5}

features to be noticed are: (1) the remarkable decrease in decomposition as the dilution increases, the value dropping from 40% of the total sulphur to 0% as the dilution is raised from 0·7 to 77; (2) corresponding increase in hydrolysis from 54 to 90%; (3) the inappreciable effect of dilution on thionization.

In the second series of experiments (Table II) glycerine was employed along with the alkali. The object of using glycerine had been to prevent

TABLE II

Effect of Dilution of Sulphur Chloride on Hydrolysis by 2N Alkali in presence of 10% Glycerine

No. of experiment	1	2	3	4
* Sulphur chloride ..	9·61	9·61	9·61	9·61
† Dilution at hydrolysis ..	0·5	1·0	2·5	5·0
* Sulphide ..	1·86	1·99	1·73	2·01
* Thiosulphate ..	1·74	1·92	2·21	1·89
* Sulphite ..	2·43	2·41	2·12	2·47
* Sulphur (found) ..	3·52	3·24	3·46	3·37
* ,, (calculated) ..	3·45	3·18	3·38	3·27
% Hydrolysis ..	38·7	41·4	36·0	41·8
% Thionization ..	12·1	13·3	15·3	12·8
% Decomposition ..	48·8	45·0	48·0	45·6
TOTAL ..	99·6	99·7	99·3	99·2

* In Table II, the quantities of sulphur chloride and of each of the products of reaction are expressed in gram atoms of sulphur and have been multiplied by 5×10^3.

† In Table II, the dilution of sulphur chloride is expressed in grams of solvent per gram atom of sulphur as sulphur chloride and has been multiplied by 10^{-5}.

any possible oxidation of sulphite to sulphate. The glycerine, however, was found to have unexpected effects on the hydrolysis. It masked the effect of dilution on hydrolysis noticed in the first series of experiments, a ten-fold increase in dilution causing barely a 3% increase in hydrolysis and a 3% decrease in decomposition. Hydrolysis appeared to be inhibited considerably by the glycerine and decomposition correspondingly stimulated. Comparative experiments (Table III) were carried out to elucidate the influence of glycerine, the dilution of sulphur chloride at hydrolysis being the

TABLE III

Influence of Glycerine on Hydrloysis of Sulphur Chloride by Alkali

No. of experiment	1	2	3	4	5	6	7	8
Nature of experiment	No gly.	10% gly.	No gly.	5% gly.	No gly.	5% gly.	No gly.	5% gly.
* S_2Cl_2	8·93	9·6	8·93	9·1	9·01	9·01	8·85	8·85
Alkali Strength	2N	2N	0·5N	0·5N	0·2N	0·2N	0·02N	0·02N
* Trithionate	..	..	..	0·91 ?	..	0·45	0·79	0·45
* Sulphate	..	..	..	..	..	0·10	0·24	0·12
* Sulphide (corrected) ..	3·45	1·94	2·97	2·19	2·88	2·03	1·60	1·37
* Thiosulphate (corrected) ..	0·54	1·60	1·04	4·30	1·55	3·74	5·52	4·98
* Sulphite	3·72	2·54	3·15	1·16	2·77	1·29	0·19	0·14
* Sulphur (found)	1·28	3·46	1·68	1·33	1·52	1·74	1·54	1·95
* ,, (calculated).. ..	1·35	3·40	1·58	1·21	1·22	1·52	1·29	1·29
% Hydrolysis	77·3	40·4	66·5	48·1	63·9	45·1	35·2	30·1
% Thionization	4·0	11·2	7·7	31·5	11·5	26·0	40·3	36·5
% Decomposition	19·3	48·0	25·1	19·6	22·4	25·8	22·6	28·6
TOTAL ..	100·6	99·6	99·3	99·2	97·8	96·9	98·1	95·2

* In Table III the quantities of sulphur chloride and of each of the products of reaction are expressed in gram atoms of sulphur and have been multiplied by 5×10^3.

same in all the experiments. In experiment 2 it will be noticed that the proportion of glycerine is 10% while in experiments 4, 6 and 8, 5% glycerine has been employed. Owing to the higher concentration of glycerine in experiment 2, the hydrolysis is less and decomposition greater than in the other experiments though owing to the higher concn. of alkali in experiment 2, the percentage hydrolysis should have been greater. In presence of glycerine (excepting at the very small alkali concentration of experiment 8) thionization is promoted, it being 2 to 4 times that in absence of glycerine.

The interesting results obtained with glycerine prompted the author to try the influence of brucine on hydrolysis of sulphur chloride by alkali. Brucine, even in traces, has been found to have a remarkable inhibiting effect on the atmospheric oxidation of sulphite. Young[49] found that in alkaline solutions 0·000,005 M brucine hydrochloride reduced the velocity to one hundredth of the normal rate. About 3 milligrams of brucine were used with the alkali in each of the experiments (Table IV). Brucine was found to increase hydrolysis considerably, the effect being most marked at alkali concentrations upto 0·2 N. Thionization was much less, indicating that brucine inhibits the oxidation of sulphite to thiosulphate in the same manner as it reduces the oxidation of sulphite to sulphate.

The hydrolysis of sulphur chloride by baryta was also studied (Table V).

The general procedure was the same as that employed in the case of sodium hydroxide, but no cadmium hydroxide was used along with the baryta. The precipitate of barium sulphite was filtered off and washed. The sulphite was estimated by adding standard iodine solution in excess and then acidifying with weak hydrochloric acid. The filtrate containing the sulphide, thiosulphate and trithionate (if any), was treated with cadmium hydroxide and the sulphide formed estimated after filtration and washing. The thiosulphate was estimated iodometrically and the trithionate by the method already indicated. It has to be stated that the experimental errors are much greater when baryta is used for hydrolysis.

Though the alkali strength was the same in the comparative experiments with sodium hydroxide and baryta, a marked difference in the reactions was noticed. Reaction H was much less in the case of baryta, the value for hydrolysis for sodium hydroxide being over twice that for baryta in 0·5 N solutions and nearly seven times as great, when the quantity of alkali used was just sufficient to neutralise the acids liberated on hydrolysis. As is to be expected, thionization was much less with baryta, owing to the insoluble nature of barium sulphite. Since reaction H gets depressed, in the case of

TABLE IV

Influence of Brucine (3 mg.) on Hydrolysis of Sulphur Chloride by Alkali

No. of experiment	1	2	3	4	5	6	7	8
Nature of experiment	No Brucine	Brucine	No Brucine	Brucine	No Brucine	Brucine	No Brucine	Brucine
* S_2Cl_2	8·92	8·92	8·92	8·92	9·01	9·01	9·1	9·1
Alkali Strength	2N	2N	0·2N	0·2N	0·1N	0·1N	0·02N	0·02N
* Trithionate	..	..	0·24	0·33 ?	0·71	0·09	0·79	0·20
* Sulphate	..	..	0·10	..	0·30	..	0·28	..
* Sulphide (corrected) ..	3·45	3·68	2·74	3·68	1·74	2·74	1·60	3·16
* Thiosulphate (corrected) ..	0·45	0·47	2·09	1·10	5·17	1·71	5·52	1·43
* Sulphite	3·72	3·92	2·59	3·63	0·61	2·77	0·19	2·98
* Sulphur (found)	1·28	1·05	1·62	0·78	1·59	1·75	1·54	1·21
* ,, (calculated).. ..	1·39	1·19	1·64	0·95	1·78	1·80	1·29	0·89
% Hydrolysis	77·3	82·0	60·8	81·7	39·0	61·4	35·2	69·5
% Thionization	4·0	3·6	15·5	8·1	38·7	12·8	40·3	10·4
% Decomposition	19·3	15·6	24·0	11·5	23·8	26·2	22·6	17·7
TOTAL ..	100·6	101·2	100·3	101·3	101·5	100·4	98·1	97·6

* In Table IV the quantities of sulphur chloride and of each of the products of reaction are expressed in gram atoms of sulphur and have been multiplied by 5×10^3.

TABLE V

Comparative Study of Hydrolysis of Sulphur Chloride with Baryta and Sodium Hydroxide

No. of experiment	1	2	3	4	5	6	7	8
Concn. Alkali	0·5N NaOH	0·5N $Ba(OH)_2$	0·5N NaOH	0·5N Baryta	0·2N NaOH	0·2N Baryta	Theoretical amt. NaOH	Theoretical amt. Baryta
% Hydrolysis	66·5	30·9	63·2	24·9	60·8	15·3	30·5	4·6
% Thionization ..	7·7	3·8	10·4	4·3	15·5	5·3	40·0	7·6
% Decomposition	25·1	72·8	25·5	78·2	24·0	84·6	25·7	89·7
TOTAL ..	99·3	107·5	99·1	107·4	100·3	105·2	96·2	101·9

baryta, the disulphur oxide suffered much greater decomposition, the value being three times that for sodium hydroxide.

In Table VI is indicated the effect of dilution of sodium hydroxide on the three parallel reactions. A tenfold dilution of alkali (2 N to 0·2 N) causes a 5% increase in decomposition and nearly a fourfold increase in thionization, the corresponding decrease in hydrolysis being about 17%. Further tenfold dilution (0·2 N to 0·02 N) of alkali causes a 25% decrease in hydrolysis and a 25% increase in thionization.

TABLE VI

Effect of Alkali Strength on Hydrolysis of Sulphur Chloride

Alkali	2N	0·5N	0·2N	0·1N	0·02N	Alkali just required for neutralisation
% Hydrolysis ..	77·3	66·5	60·8	39·0	35·2	30·5
% Thionization ..	4·0	7·7	15·5	38·7	40·3	40·0
% Decomposition ..	19·3	25·1	24·0	23·8	22·6	25·7
TOTAL ..	100·6	99·3	100·3	101·5	98·1	96·2

To study the effect of temperature on the three reactions, comparative experiments were carried out at 0° C. and at 25° C. (Table VII) the sulphur chloride dilution being kept constant. There was in general a 5% increase in hydrolysis and a corresponding decrease in decomposition when the temperature was raised from 0° to 25°C.

TABLE VII

Effect of Temperature Increase on the Hydrolysis of Sulphur Chloride by Alkali

No. of experiment	1	2	3	4	5	6
Alkali Concn.	2N	2N	0·2N	0·2N	0·02N	0·02N
Temperature	0°	25°	0°	25°	0°	25°
% Hydrolysis	78·6	83·7	55·1	60·8	30·8	35·2
% Thionization	2·6	3·0	14·5	15·5	39·2	40·3
% Decomposition	20·4	14·0	30·0	24·0	26·6	22·6
TOTAL ..	101·6	100·7	99·6	100·3	96·6	98·1

The view that during hydrolysis of sulphur chloride, thiosulphate is mainly produced by the reaction between sulphite and disulphur oxide, obtained support from the following experiments:—Hydrolysis by 0·1 N alkali was carried out in presence of 10 c.c. of formalin (40%) and the results compared with those obtained when no formaldehyde was used. The formaldehyde was expected to bind the sulphite and thus suppress thiosulphate formation. Owing to the presence of the aldehyde the sulphite could not be estimated iodometrically and had to be determined gravimetrically in the following way : sodium carbonate was added to an aliquot of the solution in a paltinum dish and the contents evaporated to dryness. The dish was then heated by a Meker burner, a little nitre being used to complete the oxidation of sulphite and thiosulphate to sulphate. The sulphate was then estimated by the microanalytical method of Pregl, and the sulphite value obtained, taking into account the thiosulphate present in the original solution.

TABLE VIII

Effect of Formaldehyde on Hydrolysis of Sulphur Chloride by 0·1 N Sodium Hydroxide

	No Formalin	Formalin present
% Hydrolysis ..	39·0	57·7
% Thionization ..	38·7	3·7
% Decomposition	23·8	33·5
TOTAL ..	101·5	94·9

The fact that reaction T is one of the three parallel reactions was indirectly confirmed by carrying out hydrolysis with 0·2 N alkali in presence of a known amount of freshly prepared sodium sulphite (6×10^{-5} g. atom of S per g. of CCl_4 soln.). In calculating sulphite produced by hydrolysis, the sulphite originally added was deducted from the sulphite found in solution after hydrolysis. The experiment (Table IX) showed that owing to the larger concentration of sulphite, greater thionization took place.

TABLE IX

Alkali	0·2 N NaOH	0·2 N NaOH + Sulphite
% Hydrolysis	60·8	59·7
% Thionization	15·5	24·4
% Decomposition	24·0	15·8
TOTAL ..	100·3	99·9

Whether the sulphur liberated in the reaction would unite with sulphite and produce thiosulphate was determined by the following experiments. A quantity of 75 % saturated solution of sulphur in carbon tetrachloride was added to the sulphur chloride in expts. 2 and 3 and the same quantity of pure carbon tetrachloride added to the sulphur chloride solution in experiment 1. 2 N alkali was used for hydrolysis. Results are indicated in Table X.

TABLE X

No. of experiement	1	2	3
		Extra sulphur	Extra sulphur
% Hydrolysis	84·9	83·3	85·5
% Thionization	3·5	3·5	3·7
% Decomposition	11·0	12·0	11·0
TOTAL	99·4	98·8	100·2

Sulphur is known to react with alkali to yield sulphide and thiosulphate in terms of the following equation :

$$4\,S + 6\,NaOH = 2\,Na_2S + Na_2S_2O_3 + 3\,H_2O$$

(Tartar and Davies,[44] Bullock and Forbes[5]). The possibility of sulphur formed in reaction D uniting with alkali to yield sulphide and thiosulphate was therefore examined. It was found that under the conditions of the present investigation, there was no measurable reaction between the sulphur and alkali.

Experiments were also carried out to determine if reaction D ($2S_2O = 3\,S + SO_2$) was reversible. A sulphur dioxide solution in carbon tetrachloride (corresponding to ten times the sulphur content of the stock solution of sulphur chloride) was mixed with an equal volume of a saturated solution of sulphur in dry carbon tetrachloride and the liquid kept for 24 hours in a dry bottle and then shaken with 2 N sodium hydroxide. Neither sulphide nor thiosulphate was formed in detectable quantities.

Solutions of hydrogen sulphide and sulphur dioxide in carbon tetrachloride were mixed together and shaken with dilute alkali and the carbon tetrachloride and aqueous layers analysed. No measureable quantity of free sulphur or thiosulphate was found. This experiment is of importance as showing that the production of free sulphur or of thiosulphate in sulphur chloride hydrolysis cannot be due to any interaction between hydrogen

sulphide and sulphur dioxide that might primarily be formed in sulphur chloride hydrolysis.

Bassett and Durrant[3] have found that the sulphide and sulphite of sodium can co-exist in alkaline solutions without any interaction taking place. It is known however, that sodium hydrogen sulphide and sodium hydrogen sulphite do interact to yield thiosulphate in terms of the following equation as pointed out by Foerster and Mommsen :[10]

$$2\,NaHS + 4\,NaHSO_3 = 3\,Na_2S_2O_3 + 3\,H_2O \text{ (Reaction T')}.$$

This raised the possibility that in the hydrolysis of sulphur chloride by alkali, the hydrogen sulphide and sulphur dioxide produced in reaction H might form momentarily, at the carbon tetrachloride interface with the aqueous solution, the two acid salts in view of the production of hydrochloric acid during hydrolysis. It was deemed advisable therefore to obtain an idea of the speed with which reaction T' takes place. The following experiments were carried out :

To 20 c.c. of freshly prepared 0·1 N NaHS solution was added 20 c.c. of freshly made 0·2 N $NaHSO_3$ solution. The mixture was kept at 25° C. for 10 minutes to allow reaction T' to take place. The reaction was then stopped by the addition of 10 c.c. of 2 N sodium hydroxide. Cadmium hydroxide was added to precipitate the residual sulphide and the filtrate titrated with iodine after addition of formaldehyde and acetic acid. If the reaction T' had been completed in 10 minutes, thiosulphate corresponding to 30 c.c. of 0·1 iodine would have been formed. Actually 7·4 c.c. of 0·1 N iodine were required for the titration of the thiosulphate. When 5% glycerine had been added to the solution of the two salts at the start of the reaction T', the titration value was 7·2 c.c., time of reaction being 10 minutes as in the previous experiment. With brucine (3 mg.) it was 6·4 c.c. and when formalin was employed the value was 0·15 c.c. These experiments show that the reaction T' is comparatively slow and that its velocity is influenced by reagents like brucine. It may therefore be concluded that reaction T' is not of any significance in the formation of thiosulphate in the sulphur chloride hydrolysis experiments.

Discussion

In discussing the hydrolysis of sulphur chloride (in carbon tetrachloride solutions) under the influence of aqueous sodium hydroxide it has to be pointed out that the reaction is very rapid even when exceedingly dilute solutions of the chloride are employed. The yellow colour of the carbon tetrachloride solution disappears within a minute or two when the chloride solution is shaken up with the alkali. Absence of sulphur chloride in the

carbon tetrachloride layer can be confirmed by withdrawing the solvent, drying it rapidly with phosphorous pentoxide and testing with dry potassium iodide. No violet colour (due to iodine) develops if the sulphur chloride has completely reacted. This sensitive reaction, it may be stated, is not only suitable for the detection of traces of sulphur chloride but can also be employed for the colorimetric estimation of small quantities of the chloride. The test is far more satisfactory than the one proposed by Castiglioni[6] in which a violet colour develops when the sulphur chloride solution is added to an ammoniacal solution of alcohol. By applying the sensitive potassium iodide test described above, it was confirmed that the reaction between dilute sulphur chloride solutions and alkali was complete, well within two minutes. The rapidity of reaction is of importance as it considerably minimises the secondary reactions that possibly can take place in the system. It may be stated that with a view to cut down secondary effects, the filtration and the analysis of the aqueous layer was carried out as rapidly as possible and scarcely took more than 20 minutes.

Owing to the use of cadmium hydroxide, the sulphide produced in reaction H (Hydrolysis) is quickly immobilised and does not take part in secondary reactions. The removal of sulphide eliminates for instance, the catalytic influence the sulphide would otherwise have exerted on the thionization of sulphite by free sulphur liberated during the reaction (Hargreaves and Dunnigham[16], Watson and Rajagopalan[48], Bassett and Durrant[3]).

Besides reaction H, the decomposition of thiosulphuric acid under favourable pH conditions can produce sulphide :

$$2\,H_2S_2O_3 = H_2S + H_2S_3O_6$$

$$H_2S_2O_3 + H_2O = H_2S + H_2SO_4$$

Both these types of decomposition occur to a small extent when very dilute alkali is used for sulphur chloride hydrolysis. As already stated a suitable correction has been applied for sulphide values in such cases. The sulphide therefore correctly represents the magnitude of reaction H.

It will be noticed that sulphite is in excess of sulphide when alkali concentration is greater than 0·2 N but on the other hand is lower than sulphide produced when more dilute solutions of alkali are employed for hydrolysis. If reaction H was the only one taking place, the sulphite obtained should equal the sulphide. It has already been pointed out that under the conditions of hydrolysis, the hydrogen sulphide and sulphur dioxide produced by reaction H do not interact to yield sulphur or thiosulphate by the following reactions :

$$2\,H_2S + SO_2 = 3\,S + 2\,H_2O$$

$$2\,NaHS + 4\,NaHSO_3 = 3\,Na_2S_2O_3 + 3\,H_2O$$

It is therefore to be concluded that in the case of hydrolysis by stronger solutions of alkali there is some reaction producing sulphite in excess of sulphide and that when the alkali is dilute, the deficiency of sulphite is due to its removal as a result of some reaction. Reaction D (Decomposition) and reaction T (Thionization) have been found to be responsible for the observed difference between sulphite and sulphide values.

The decomposition of disulphur oxide (Reaction D) seems to be governed largely by dilution. In expt. 7 (Table I) it dropped to zero while in expts. 1 and 2 it was over 40% of the disulphur oxide primarily formed. The decomposition is due to a reaction between two S_2O (or $H_2S_2O_2$) molecules :

$$S_2O + S_2O = 3\,S + SO_2$$

$$\text{or } H_2S_2O_2 + H_2S_2O_2 = 3\,S + H_2SO_3 + H_2O.$$

The extent of reaction D seems to be determined by the frequency of fruitful collisions between S_2O molecules. This frequency is dependent on the proximity between two S_2O molecules when they are formed by hydrolysis. The concentration of sulphur chloride (the source of the disulphur oxide) therefore determines the extent of reaction D. If the reaction is to be eliminated during hydrolysis (*cf.* expt. 7, Table I) it seems to be necessary (when 2 N alkali is used) to have in solution a molecular ratio of sulphur chloride to carbon tetrachloride of the order of 1 : 100,000.

Reaction T (Thionization) seems to be mainly responsible for the formation of thiosulphate. It has already been pointed out that under the experimental conditions of this investigation, no measurable amount of thiosulphate is produced either by the reaction between hydrogen sulphide and sulphur dioxide or by the reaction between free sulphur and sodium sulphite. On the other hand there is definite evidence (which has already been indicated) that part of the sulphite produced in reaction H is converted into thiosulphate. The powerful thionizing agent responsible for this oxidation of sulphite seems to be disulphur oxide. Sulphite thionization seems to be considerable when alkali concentration is low, as can be gathered from the small sulphite concentrations (in comparison with corresponding sulphide values) in such experiments (Table III, expts. 7 and 8, Table IV, expts. 5 and 7).

Besides reaction T, the following reaction D′ can possibly form thiosulphate :

$$2\,S_2O + 2\,NaOH = Na_2S_2O_3 + 2\,S.$$

This reaction may be considered to be taking place in two steps :

$$2\,S_2O = S_2O_2 + 2\,S \quad (a)$$

$$S_2O_2 + 2\,NaOH = Na_2S_2O_3 + H_2O \quad (b)$$

The difference between reactions T and D′ is that in the former case the sulphur liberated in step (*a*) is assumed to thionize sulphite to thiosulphate while in D′ elementary sulphur is actually liberated. Reaction T therefore involves the participation of sulphite. When barium hydroxide is used, or when formalin is added to the sodium hydroxide employed in hydrolysis, the sulphite is immobilised and reaction T cannot take place. A small quantity of thiosulphate however is still formed (Tables V and VIII) and it is therefore to be concluded that reaction D′ does occur to a slight extent. While S_2O is necessary for thiosulphate formation from sulphite, the latter is not at all required for conversion of S_2O into thiosulphate in terms of reaction D′. It may be pointed out that in the case of hydrolysis of sulphur chloride by moderately strong solutions of alkali, it is possible to represent the chemical phenomenon by reactions H, D′ and D (without introducing reaction T) but in cases of hydrolysis by dilute alkali, reaction T cannot be ignored in any quantitative interpretation of the hydrolysis.

It is difficult to estimate reaction D′ as separately occurring from the reaction T and so, as an approximation, it has been assumed that only one reaction, namely T, is responsible for the production of thiosulphate. This assumption raises the values for reaction D by a few per cent., as the sulphur produced in D′ is attributed to reaction D.

The sulphur produced by reaction D is entirely found in carbon tetrachloride solution, when alkali concentration is at least 0·5 N. This is significant in view of the fact that sulphur produced by the interaction between hydrogen sulphide and sulphur dioxide in presence of water is principally as $S\mu$ (Brownlee[4]). This lends indirect support to the view that in sulphur chloride hydrolysis the sulphur is not the product of any reaction between hydrogen sulphide and sulphur dioxide. No doubt alkaline solutions have been found to hasten the conversion of amorphous sulphur into the ordinary soluble sulphur (Smith and Brownlee;[41] McKee[25]) and there is therefore the possibility that elementary sulphur liberated in hydrolysis is in the first instance amorphous and is converted into ordinary sulphur under the catalytic influence of the alkali. The rate of conversion of amorphous sulphur into ordinary sulphur has been studied by the present author and he finds that this is not fast enough to account for the formation, in the course of the hydrolysis experiments (whose duration was 15 to 20 minutes) of sulphur entirely soluble in carbon tetrachloride.

When dilute alkali is used for hydrolysis, an appreciable amount of the liberated sulphur is in the amorphous condition. It is also found that in such cases there is thionate formation as well. Both the production of

amorphous sulphur and the formation of thionate seem to be due to the decomposition of thiosulphuric acid in cases of hydrolysis by dilute alkali, owing to the fact that the hydrolysis of sulphur chloride is accompanied by the liberation of hydrochloric acid which produces at the interface between carbon tetrachloride and water local zones of acidity conducive to the decomposition of thiosulphuric acid.

The decomposition of thiosulphuric acid has been a subject of extensive investigation (Bassett and Durrant,[3] Deines,[8] Reisenfeld and Sydow,[37] Schaffer and Böhm,[39] Kurtenacker and Ivanov,[22] Râyand Maulick,[36] Hansen,[14] Foerster and Umbach[11]). Three reactions are possible:

$$H_2S_2O_3 = H_2SO_3 + S$$
$$2\,H_2S_2O_3 = H_2S + H_2S_3O_6$$
$$H_2S_2O_3 + H_2O = H_2S + H_2SO_4.$$

The first of these three reactions probably accounts for part of the amorphous sulphur, the second for the presence of thionate and the third for the presence of sulphate in certain hydrolysis experiments. Smith and Brownlee[41] have found that the sulphur precipitated by the addition of acid to sodium thiosulphate is in the first instance 100% amorphous sulphur. The presence of sulphate in the products of hydrolysis is not likely to be due to atmospheric oxidation of sulphite, for it would then have been produced in all cases of hydrolysis though, to a varying degree owing to the influence of alkali on sulphite oxidation (Kolthoff and Furman).[19] Production of sulphate, owing to auto-reduction or auto-oxidation of sulphite (*cf.* Mellor,[26] Kurtenacker and Kaufmann,[23] Foerster and Hornig[9]) can also be ignored in the present investigations as the analysis of the aqueous layer was carried to completion within 20 minutes of the actual hydrolysis of sulphur chloride.

It will be noticed that it has been assumed that the thionate found is entirely as trithionate. That thionates higher than the trithionate are formed in thiosulphuric acid decomposition has often been suggested, but even if this be the case, the higher polythionates will readily decompose in alkaline media and finally give trithionate (Hansen[15]). Hansen points out that even the trithionate is not very stable and gives sulphate in acid and weakly alkaline solutions and sulphite in solutions more alkaline than 1 N. The decomposition of trithionate yielding sulphite, introduces a small error in the calculation of the reactions H, T and D, for which it is not practicable to apply a suitable correction. Such decomposition, however, takes place only in strongly alkaline solutions, but in such solutions the formation of trithionate is itself unlikely.

Investigations on sulphur chloride by several authors have indicated that S_3Cl_2 and S_2Cl_4 possibly exist in sulphur chloride (Lowry, McHatton and Jones,[24] Trautz,[46] Baroni,[2] Spong[42]). The presence of these chlorides however, does not vitiate the consideration of sulphur chloride hydrolysis as being made up of the three reactions H, T and D, for the hydrolysis of these impurities in sulphur chloride may be pictured as follows :

$$S_3Cl_2 + H_2O = S + S_2O + 2\,HCl$$
$$S_2Cl_4 + 2\,H_2O = 2\,S + SO_2 + 4\,HCl.$$

The experimental errors inherent in the analysis of sulphur and the different sulphur compounds produced by hydrolysis may now be discussed. The error in the estimation of sulphur, in carbon tetrachloride solutions was not more than 2% (*cf.* Rao, B. S. and Rao, M. R. A.,[34]), at the concentrations met with in these investigations. Amorphous sulphur, formed as a suspension in aqueous medium could not be accurately estimated.

The estimation of sulphide was quite satisfactory except in cases where hydrolysis had been effected by dilute alkali (0·1 N) wherein appreciable errors were caused by the adsorption of sulphite. Experiments were carried out to determine the extent of adsorption of sulphite by the cadmium sulphide and cadmium hydroxide precipitates. No measurable adsorption of sulphite took place in solutions above 0·1 N in alkalinity, but in feebly alkaline solutions 2 to 3% of the sulphite present was brought down by the sulphide precipitate. Even on prolonged washing with water the adsorbed sulphite could not be removed. 0·2 N alkali however was much more effective in the removal of adsorbed sulphite. It has to be pointed out that when cadmium sulphide containing sulphite is treated with iodine in presence of acid, both sulphide and sulphite react with iodine exclusively, and the interaction between sulphide and sulphite is negligible. In experiments with baryta, it was noticed that there was appreciable adsorption of sulphide by the barium sulphite precipitate. This probably accounts for the much greater experimental error noticed in hydrolytic experiments with baryta.

Owing to the fact that in the iodometric estimation of thiosulphate 2 atoms of sulphur correspond to an atom of iodine (while for sulphite and sulphide 0·5 atom of the element corresponds to an iodine atom) the experimental error in the estimation of thiosulphate is proportionately greater. In the calculation of free sulphur by the relationship :

$$S = \text{Thiosulphate} + 3\,(\text{sulphite} - \text{sulphide})$$

any experimental error in the estimation of sulphite or sulphide gets considerably magnified in computing the sulphur value. In some of the earlier hydrolysis experiments (Table I) the agreement between sulphur (found)

and sulphur (calculated) is not satisfactory, but in later experiments the agreement was far more satisfactory, except in cases where the inherent experimental errors due to adsorption and other causes, were much greater.

The highly unstable sulphur iodide (whose existence has been questioned in the past) has been prepared in this laboratory by M. R. A. Rao by the action of dry potassium iodide on sulphur chloride solutions (Rao, M. R. A.[35]). He has studied the hydrolysis of sulphur iodide by modertately strong solutions of alkali and it is of interest to compare the values for the reactions H, T and D obtained with the two halides of sulphur. In his paper (sent for publication) results of hydrolysis of sulphur iodide have been expressed in terms of reactions H, D′ and D of the present paper. Since then, it has been found necessary to introduce reaction T in place of D′ to explain the results of hydrolysis by dilute alkali. In Table XI, the values obtained by M. R. A. Rao have been recalculated on the basis of the reactions H, T and D.

TABLE XI

Comparative Study of the Hydrolysis of Sulphur Iodide and Sulphur Chloride by 2 N Sodium Hydroxide at Different Dilutions

	Sulphur Iodide Hydrolysis				Sulphur Chloride Hydrolysis		
Dilution ..	8·5	18·1	42·5	162·4	3·8	38·7	77·1
% Hydrolysis ..	1·4	2·3	6·8	26·6	75·8	88·6	90·4
% Thionization ..	14·2	15·7	18·3	13·5	9·6	8·1	9·7
% Decomposition ..	82·1	78·2	75·1	53·1	15·9	3·1	0·0
TOTAL	97·7	96·2	100·2	93·2	101·3	99·8	100·1

If disulphur oxide is the primary product of hydrolysis of the sulphur halides by alkali, it may be expected that the values for the three parallel reactions should approximately be the same for corresponding dilutions of iodide and chloride. Further work on sulphur iodide is undoubtedly needed before the marked differences in results of hydrolysis can be explained satisfactorily, but at present two possible explanations may be offered. One explanation is that sulphur iodide exists in a ploymerized condition, in carbon tetrachloride solutions even at great dilutions. The effect of such polymerisation is to increase the proximity between S_2O (or $H_2S_2O_2$) molecules formed by hydrolysis of the iodide, thus rendering greater, the chances of decomposition in terms of reaction D. Owing to the great instability of sulphur iodide, it has not yet been possible to determine in this laboratory the molecular

weight of the iodide by cryoscopic methods. It is very probable, however, that sulphur iodide molecules are polymers of S_2I_2. It may be mentioned that appreciable polymerization has been noticed in the case of sulphur chloride, in carbon tetrachloride solutions by Patrick and Hackerman.[31]

Another possible explanation is that the structure of the sulphur iodide molecule is markedly different from that of the molecule of sulphur chloride. Several experimental investigations have in recent years been carried out on the structure of sulphur chloride. From a study of the reactions of the complex $AlCl_3 2S_2Cl_2$, Ruff and Golla[38] favoured the structure $S:S(:Cl_2)$. The same structure has been assigned to the chloride by Trivedi[47] from his work on absorption spectra. Electron diffraction studies by Ackerman and Mayer[1] however, have given evidence of the structure Cl.S.S.Cl. Scheibe and Stoll[40] favour the structure RO–SS–OR for esters of thiosulphurous acid as a result of Raman spectra and dipole moment investigations. To determine the structure of the hypothetical thiosulphurous acid and of its chloride S_2Cl_2, Giacomello[13] studied the behaviour of sulphur chloride solutions in benzene towards phenols and concluded that sulphur chloride is an equilibrium mixture of $S:S(:Cl_2)$ (Structure A) with Cl–S–S–Cl (Structure B) and that the latter form is stabler and is in greater proportions in the mixture. Structure A was considered by him to indicate a more reactive form of the chloride than B. When sulphur halides are hydrolysed, we may therefore expect to get as the primary products the two forms of thiosulphurous acid corresponding to structures A and B of sulphur chloride. The proportion of the two forms, in the thiosulphurous acid obtained, is likely to depend on the relative amounts of A and B originally present in the halide. Sulphur chloride is known to have form B in excess and if it be assumed that in sulphur iodide form A preponderates the greater decomposition noticed in sulphur iodide hydrolysis can be explained. Experimental determination of the structure of sulphur iodide, by suitable methods, may therefore be expected to throw light on the observed difference in the hydrolysis of the two halides of sulphur.

Finally the question whether disulphur oxide or thiosulphurous acid is the primary product of sulphur chloride hydrolysis, may be considered. From theoretical considerations it is obvious that thiosulphurous acid would be formed first, by the hydrolysis of sulphur chloride. But the question is whether the unstable acid acts as such in the three reactions H, T and D or whether it splits off water and forms disulphur oxide before undergoing further transformation. In spite of the increasing attention that has been paid to thiosulphurous acid and its alkyl derivatives in recent years, the acid still continues to be a hypothetical substance (Meuwsen[27], Hellmuth[18], Stamm

and Wintzer[43]). Owing to the presence of the elements of water in the molecule, thiosulphurous acid seems to be extremely unstable and it is only when the molecule is rendered less active by replacing the hydrogen by an alkyl group that stability is secured. Disulphur oxide, on the other hand, has actually been prepared in the form of a solution in carbon tetrachloride (B. S. Rao[33]) and until we have definite evidence of the existence of thiosulphurous acid in the free state, it is perhaps appropriate to look upon disulphur oxide as the primary product of the hydrolysis of sulphur chloide. Judging however, from the difference in behaviour on hydrolysis between sulphur chloride and sulphur iodide, and also between sulphur chloride and disulphur oxide (Part II of these studies) there is reason to believe that at least a part of the thiosulphurous acid formed by hydrolysis of sulphur halides, reacts as such without splitting off water (to give rise to disulphur oxide). The precise nature of the primary product has therefore to be left open for the present, but the experimental work described in this paper makes it clear that the primary product is either disulphur oxide or its hydrate the hypothetical thiosulphurous acid. The fact that disulphur oxide has been prepared, it may be claimed, has made the existence of thiosulphurous acid itself, more probable.

Summary

(1) The hydrolysis of sulphur chloride has been studied by carrying out the reaction at the interface between very dilute solutions of the compound in carbon tetrachloride and aqueous alkali, in presence of cadmium hydroxide, The alkali and the cadmium hydroxide circumscribed the scope of secondary reactions and rendered possible a quantitative interpretation of the phenomenon.

(2) The products of hydrolysis were free sulphur, sulphide, sulphite and thiosulphate, and were estimated by suitable analytical methods. The free sulphur was mostly present in the carbon tetrachloride layer. When dilute alkali was used for hydrolysis, a part of the sulphur appeared in the amorphous condition, and sulphate and trithionate were formed in small quantities, owing to decomposition of thiosulphuric acid.

(3) The results can most satisfactorily be explained on the basis that disulphur oxide (if not its hydrate—the hypothetical thiosulphurous acid) is the primary product of hydrolysis. Disulphur oxide has now been obtained in carbon tetrachloride solutions. The oxide undergoes three parallel reactions: (*a*) hydrolysis, producing sulphite and sulphide in equimolecular proportions, (*b*) thionization, oxidising part of sulphite formed in hydrolysis to thiosulphate and (*c*) decomposition yielding, sulphur and sulphite:

$S_2O + 4\,NaOH = Na_2S + Na_2SO_3 + 2H_2O$ (Reaction H) Hydrolysis.

$2\,Na_2SO_3 + 2\,S_2O + 2\,NaOH = 3\,Na_2S_2O_3 + H_2O$ (Reaction T) Thionization.

$2\,S_2O + 2\,NaOH = 3\,S + Na_2S_2O_3 + H_2O$ (Reaction D) Decomposition.

(4) A method of calculating the extent of each of the three reactions from the analytical values of the products of hydrolysis, is indicated and it is shown that: Free Sulphur = Thiosulphate + 3 (Sulphite − Sulphide).

(5) The effect on hydrolysis, exercised by dilution of sulphur chloride, has been studied and found to be to increase reaction H and reduce D. When the molecular ratio of sulphur chloride to carbon tetrachloride is of the order of 1 : 100,000, reaction D drops to zero (2 N alkali being used for hydrolysis).

(6) Glycerine added to the alkali, has been found to reduce H and increase D and T; while brucine, even in small quantities, increases H and inhibits T.

(7) Hydrolysis by baryta has been found to be markedly different from that by sodium hydroxide. With baryta, hydrolysis and thionization are less but decomposition much more than with sodium hydroxide.

(8) Dilution of sodium hydroxide affects the three reactions differently. Hydrolysis diminishes, there is a small increase in decomposition, while thionization markedly increases.

(9) The effect of an increase in temperature on the three reactions is comparatively small.

(10) There is evidence to show that production of thiosulphate is to a certain extent due to the following reaction:

$$2\,S_2O + 2\,NaOH = Na_2S_2O_3 + 2\,S$$

for, when sulphite is immobilised by the use of baryta or of formalin, thiosulphate is still produced, though to a much smaller extent.

(11) It is shown that sulphur and thiosulphate are not obtained as a result of any secondary reactions but are directly formed from the disulphur oxide.

(12) The behaviour of sulphur iodide (which has been prepared in this laboratory in carbon tetrachloride solutions) is compared with that of sulphur chloride towards alkali and tentative explanations are offered for the observed difference.

The author wishes to thank Mr. M. R. A. Rao for his valuable assistance in carrying out part of the analytical work.

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RAMAN AND INFRA-RED SPECTRA OF CYCLOPROPANE

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Received November 28, 1939

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

The spectrum of cyclopropane has been observed by Lespieau, Bourgel and Wakeman (1932), Kohlrausch and Köppel (1934), Ananthakrishnan (1937) and Harris, Ashdown and Armstrong (1936) in the Raman effect and by Bonner (1937) and Linnet (1938) in the infra-red. The polarisation of the Raman lines has been observed by Ananthakrishnan (1937). In the present investigation the data adopted as the basis of the theoretical discussion are those of Ananthakrishnan in the Raman effect and of Linnet in the infra-red. As Raman spectrum pictures of cyclopropane taken by Ananthakrishnan were available in the laboratory, the author has carefully examined his plates. The results of Ananthakrishnan as well as those observed on further examination of his plates, are reproduced in the table below. Infra-red

Table I

Infra-red ..	..	..	826	860 (*v.s.*)	886	1041 (*s*)	..	..
Raman ..	736 (*o b.d.*) D	..	..	863 (8 *b.*) D	..	..	1187 (15) P	..
Infra-red ..	1425	1435 (*m.s.*)	1445	..	..	..	..	1739 (*m.*)
Raman ..	..	1435 (2 *b.*) D (doublet)	..	1454 (0) P	..	1472 (0) P	1503 (0) P	..
Infra-red ..	1779 (*w.*)	..	2083 (*m.s.*)	2179 (*w.*)	..	2331 (*w.*)	2494 (*m.w.*)	2632 (*w.*)
Raman ..	..	..	..	..	..	..	..	..
Infra-red ..	..	..	..	..	..	..	3049 (*v.s.*)	..
Raman ..	2852 ($\frac{1}{2}$) P	..	2952 (1) P	3010 (10) P	..	3028 (10) P	..	3086 (6 *b. d.*)
Infra-red ..	3846 (*w.*)	..	4348 (*m.w.*)	..	..	5130 (*v.w.*)	6021 (*w.*)	..

frequencies observed by Linnet, and the state of polarisation of the Raman lines are stated in Table I.

The frequencies 1454 (0), 1472 (0) have been observed by the author on Ananthakrishnan's plates and both these lines are polarised. The lines 1022 and 1873 reported by Harris, Ashdown and Armstrong in the Raman spectrum of cyclopropane are not present on the plates of Ananthakrishnan although much weaker lines like 1454 (0), 1503 (0) reported by the above authors are present there. These lines have therefore been left out. It is difficult to say with certainty about the presence of the very weak line at 382 reported by the above authors ; in Ananthakrishnan's plates also there appears to exist a very faint concentration of intensity in the neighbourhood of 400 cm.$^{-1}$

No satisfactory explanation of the Raman and infra-red lines in cyclopropane has as yet been given. Polarisation measurements and the strong intensity of the lines have enabled Ananthakrishnan to identify the lines 1187 and 863 as the ring frequencies of the molecule. Bonner (1937) has calculated the values of C–C force constant (k_1) and of $\overset{\overset{C}{\diagup}}{C}$–C deformation ($k_3$) by taking three CH_2 groups arranged at the corners of an equilateral triangle. He finds

$$k_1 = 4{\cdot}04 \times 10^5 \text{ dynes}, \quad k_3 = -\cdot 084 \times 10^5 \text{ dynes}.$$

It is the purpose of this paper to present a complete explanation of the Raman and infra-red spectra of cyclopropane based on the numerical calculation of frequencies by the group theory method.

2. *Molecular Structure and the Symmetry of the Molecule*

Pauling and Brockway (1937) have made an electron diffraction study of the molecule of cyclopropane. The authors take as the molecular model (Fig. 1) a regular triangle of three carbon atoms, the hydrogen atoms lying at tetrahedron corners out of the plane of carbon rings. The hydrogen atoms H_4, H_5, H_6, marked O in the figure, form one equilateral triangle above the

○ H_4, H_5, H_6 } Hydrogen atoms
● H_7, H_8, H_9 }
○ C_1, C_2, C_3—Carbon atoms

FIG. 1

plane of carbon atoms and H_7, H_8, H_9, marked ● in the figure, form another below the plane of carbon atoms. The X, Y co-ordinates of atom pairs (4, 7), (5, 8) and (6, 9) are the same, the Z co-ordinate being equal in magnitude but opposite in sign. According to these authors, the C–C distance

in cyclopropane is $1{\cdot}53 \pm {\cdot}03°$ A and the C–C angle is 60°.

The molecule belongs to the symmetry class D_{3h} and possesses the following elements of symmetry :

(1) a double axis of three fold rotation ($2\,C_3$) ;

(2) a double axis of three fold rotation-reflection ($2\,S_3$) ;

(3) three two-fold axes of rotation ($3\,C_2$) passing through one carbon atom each ;

(4) three planes of symmetry ($3\,\sigma_v$) each containing one atom of carbon and two atoms of hydrogen ;

(5) a plane of symmetry σ_h containing three carbon atoms ;

(6) an identity E.

Using the character table II it is possible to calculate the number and nature of modes of vibrations and the selection rules in the Raman effect and

TABLE II. THE CHARACTER TABLE

D_{3h}	E	$2\,S_3$	$2\,C_3$	$3\,C_2$	σ_h	$3\sigma_v$	Total number of vibrations	Internal vibrations		Translation and Rotation	Selection rule	
								Molecule	Ring		Raman	Infa-red
A A_1' ..	1	1	1	1	1	1	3	3	1	0	pol.	*f*
B A_2'' ..	1	−1	1	−1	−1	1	3	2	0	1 (Q_z)	*f*	*a*
C A_2' ..	1	1	1	−1	1	−1	2	1	0	1 (Q_{wz})	*f*	*f*
D A_1'' ..	1	−1	1	1	−1	−1	1	1	0	0	*f*	*f*
E_1 E' ..	2	−1	−1	0	2	0	5	4	1	1 (Q_x, Q_y)	dep.	*a*
E_2 E'' ..	2	1	−1	0	−2	0	4	3	0	1 (Q_{wx}, Q_{wy})	dep.	*f*
a_R ..	9	0	0	1	3	3						
ϵ(R) ..	21	0	0	3	3	9	for internal vibrations					
ϵ(R) ..	27	0	0	−3	3	9	for all vibrations including translations and rotations					

infra-red, according to the rules given by Wigner (1930). The number of oscillations a_ρ of type ρ is given by $a_\rho = \frac{1}{h}\Sigma\chi^{(\rho)} \epsilon$ (R)

where

$$\epsilon(R) = \underset{\text{rotation pure}}{\Sigma(u_R - 2)(1 + 2\cos\phi)} + \underset{\text{rotation and reflection}}{\Sigma'' u_R (2\cos\phi - 1)}$$

h is the number of elements of symmetry for a particular group, ϕ is the angle of rotation involved in a symmetry operation of the group, u_R is the number of invariant points in any symmetry operation and $\chi^{(\rho)}$ is the character of the irreducible representation of the various types of elements of the group.

The spectrum of cyclopropane can now be analysed qualitatively. The character table shows that there should be only three polarised lines. Actually eight polarised lines are observed, 1187, 1454, 1472, 1503, 2852, 2952, 3010 and 3028. It is possible to explain the presence of some of these lines on the basis of Fermi-resonance. The splitting of the ν (C–H) frequency into two intense lines at 3010 and 3028 may be due to the overtone of the line 1503 coinciding with the ν (C–H) frequency. Similarly the presence of two polarised lines 1472 and 1503 can be explained by supposing that the polarised δ (C–H) frequency splits because the overtone of the line 736 falls in its neighbourhood. The ν (C–H) and δ (C–H) frequencies are therefore taken as 3017 and 1487 in the present investigation. It is likely that the lines 2852 and 2952 are the overtones of the lines 1435 and 1472. This view is consistent with the weak intensity and the polarised character of these lines. 1187 is the breathing frequency of the ring. Thus the three polarised lines coming in class A are 1187, 1487, 3017.

In class B there are two vibrations which are infra-red active and Raman inactive. Strong infra-red absorptions occur at 1041 and 3049 cm.$^{-1}$. These lines may be identified with the two frequencies in this class. In the class E_1, the vibrations are both Raman and infra-red active. Of the four vibrations two may be identified with the lines 860 and 1435 both of which come out with nearly equal intensities in the Raman effect and infra-red.

It is possible now to calculate the frequencies belonging to class C_1, D_1, E_1 and E_2 by the use of symmetry co-ordinates.

3. *Symmetry Co-ordinates*

It follows from the character table that the number of symmetry modes under various representations are given by $3A + 2B + C + D + 4E_1 + 3E_2$, pure rotations and translations being excluded. It follows, therefore,

that if we use symmetry co-ordinates the determinant giving the fundamental frequencies will split into two linear, one quadratic, two cubic, and one quartic factors. So it becomes possible to solve the vibrational problem by writing down kinetic and potential energies for each factor separately. In determining the potential and kinetic energy in any mode of oscillation it is useful to express the co-ordinates of any atom referred to its equilibrium position as origin. If x_i, y_i, z_i (Fig. 1) are the co-ordinates of the i-th atom with its equilibrium position as origin, x_i points towards the centre of triangle in which the atom lies z_i is perpendicular to the plane in which the atom lies and is taken +ve upwards for hydrogens lying above the plane of carbon atoms and taken positive downwards for hydrogens lying below the plane of carbon atoms ; y_i is at right angles to both these directions and is taken positively in the direction which makes the motion right-handed.

The symmetry co-ordinates for non-degenerate modes can be written down easily from the character table, and normal co-ordinates for *translation* and *rotation* Q_x, Q_y, Q_z, $Q_{\omega x}$, $Q_{\omega y}$, $Q_{\omega z}$ can be written down directly. This enables us to write out the symmetry co-ordinates for degenerate classes as well by using the orthogonality relations between the various co-ordinates and by the help of the character table. When a symmetry co-ordinate occurs singly in a class it becomes a normal co-ordinate written as Q, but if more than one co-ordinate exist in a class, the normal co-ordinates are to be obtained as independent linear functions of the symmetry co-ordinates with coefficients which depend upon the force-constants existing in the molecule. These co-ordinates are denoted as Q′. Wherever Q′s occur with suffixes, a degeneracy is implied. The coefficient of any co-ordinate in the expression for the Q′s gives the component along that co-ordinate direction. These coefficients are proportional to the amplitude of the motions of atoms in the corresponding mode of vibration. These co-ordinates are :

$$\left.\begin{aligned} Q'_1 &\rightarrow x_1 + x_2 + x_3 \\ Q'_2 &\rightarrow x_4 + x_5 + x_6 + x_7 + x_8 + x_9 \\ Q'_3 &\rightarrow z_4 + z_5 + z_6 + z_7 + z_8 + z_9 \end{aligned}\right\} \text{A (3)}$$

$$\left.\begin{aligned} Q_z &\rightarrow M^{\frac{1}{2}}(z_1 + z_2 + z_3) + m^{\frac{1}{2}}(z_4 + z_5 + z_6 - z_7 - z_8 - z_9) \\ Q'_4 &\rightarrow 2m^{\frac{1}{2}}(z_1 + z_2 + z_3) - M^{\frac{1}{2}}(z_4 + z_5 + z_6 - z_7 - z_8 - z_9) \\ Q'_5 &\rightarrow x_4 + x_5 + x_6 - x_7 - x_8 - x_9 \end{aligned}\right\} \text{B (3)}$$

$$Q_{wz} \rightarrow \frac{2a}{\sqrt{3}} M^{\frac{1}{2}} (y_1 + y_2 + y_3) \div \left(\frac{2a}{\sqrt{3}} + b \cos\phi\right) \times m^{\frac{1}{2}} (y_4 + y_5 + y_6 + y_7 + y_8 + y_9)$$

$$Q_6 \rightarrow 2\left(\frac{2a}{\sqrt{3}} + b \cos\phi\right) m^{\frac{1}{2}} (y_1 + y_2 + y_3) - M^{\frac{1}{2}} \left(\frac{2a}{\sqrt{3}}\right) \times (y_4 + y_5 + y_6 + y_7 + y_8 + y_9) \quad \text{C (2)}$$

$$Q_7 \rightarrow y_4 + y_5 + y_6 - y_7 - y_8 - y_9 \quad \cdots\cdots \quad \text{D (1)}$$

$$Q_x \rightarrow M^{\frac{1}{2}} \{ (2y_1 - y_2 - y_3) - \sqrt{3} (x_2 - x_3) \} + m^{\frac{1}{2}} \{ (2y_4 - y_5 - y_6) - \sqrt{3} (x_5 - x_6) + (2y_7 - y_8 - y_9) - \sqrt{3} (x_8 - x_9) \}$$

$$Q_y \rightarrow M^{\frac{1}{2}} \{ (-2x_1 + x_2 + x_3) - \sqrt{3} (y_2 - y_3) \} + m^{\frac{1}{2}} \{ (-2x_4 + x_5 + x_6) - \sqrt{3} (y_5 - y_6) + (-2x_7 + x_8 + x_9) - \sqrt{3} (y_8 - y_9) \}$$

$$Q'_{8a} \rightarrow (2y_1 - y_2 - y_3) + \sqrt{3} (x_2 - x_3)$$

$$Q'_{8b} \rightarrow (2x_1 - x_2 - x_3) - \sqrt{3} (y_2 - y_3)$$

$$Q'_{9a} \rightarrow (2y_4 - y_5 - y_6) + \sqrt{3} (x_5 - x_6) + (2y_7 - y_8 - y_9) + \sqrt{3} (x_8 - x_9)$$

$$Q'_{9b} \rightarrow (-2x_4 + x_5 + x_6) + \sqrt{3} (y_5 - y_6) + (-2x_7 + x_8 + x_9) + \sqrt{3} (y_8 - y_9)$$

$$Q'_{10a} \rightarrow (z_5 + z_8) - (z_6 + z_9)$$

$$Q'_{10b} \rightarrow (-2z_4 + z_5 + z_6) - (2z_7 - z_8 - z_9)$$

$$Q'_{11a} \rightarrow 2m^{\frac{1}{2}} \{ (2y_1 - y_2 - y_3) - \sqrt{3} (x_2 - x_3) \} - M^{\frac{1}{2}} \{ (2y_4 - y_5 - y_6) - \sqrt{3} (x_5 - x_6) + (2y_7 - y_8 - y_9) - \sqrt{3} (x_8 - x_9) \}$$

$$Q'_{11b} \rightarrow 2m^{\frac{1}{2}} \{ (-2x_1 + x_2 + x_3) - \sqrt{3} (y_2 - y_3) \} - M^{\frac{1}{2}} \{ (-2x_4 + x_5 + x_6) - \sqrt{3} (y_5 - y_6) + (-2x_7 + x_8 + x_9) - \sqrt{3} (y_8 - y_9) \}$$

$\left.\begin{array}{l}\\\

$$Q_{wx} \rightarrow [m^{\frac{1}{2}} b \sin\phi \{ (-2x_4 + x_5 + x_6) - \sqrt{3}(y_5 - y_6) + (2x_7 - x_8 - x_9) + \sqrt{3}(y_8 - y_9) \} + m^{\frac{1}{2}} \left(\frac{2a}{\sqrt{3}} + b\cos\phi\right) \{ (-2z_4 + z_5 + z_6) + (2z_7 - z_8 - z_9) \} + M^{\frac{1}{2}} \frac{2a}{\sqrt{3}} (-2z_1 + z_2 + z_3)]$$

$$Q_{wy} \rightarrow [m^{\frac{1}{2}} b \sin\phi \{ (2y_4 - y_5 - y_6) - \sqrt{3}(x_5 - x_6) + (-2y_7 + y_8 + y_9) + \sqrt{3}(x_8 - x_9) \} + m^{\frac{1}{2}} \left(\frac{2a}{\sqrt{3}} + b\cos\phi\right) \{ (-z_5 + z_8) + (z_6 - z_9) \} + M^{\frac{1}{2}} a(-z_2 + z_3)]$$

$$Q'_{12a} \rightarrow 2\left[m^{\frac{1}{2}} \left(\frac{2a}{\sqrt{3}} + b\cos\phi\right) \{ (-2z_4 + z_5 + z_6) + (2z_7 - z_8 - z_9) \} + M^{\frac{1}{2}} \frac{2a}{\sqrt{3}} (-2z_1 + z_2 + z_3)\right]$$

$$-\left[\frac{m\left(\frac{2a}{\sqrt{3}} + b\cos\phi\right)^2 + M\frac{2a^2}{3}}{m^{\frac{1}{2}} b \sin\phi}\right] \left\{\begin{matrix}(-2x_4 + x_5 + x_6) - \sqrt{3}(y_5 - y_6) \\ + (2x_7 - x_8 - x_9) + \sqrt{3}(y_8 - y_9)\end{matrix}\right\} \quad \left.\begin{matrix}\\ \\ \\ \

In the above $2a$ is the length of the C–C bond, b is the length of the C–H bond, 2ϕ is the H–C–H angle, m and M are the masses of hydrogen and carbon atoms respectively.

4. *Modes of Vibration*

These modes of vibration are represented diagrammatically below (Fig. 2).

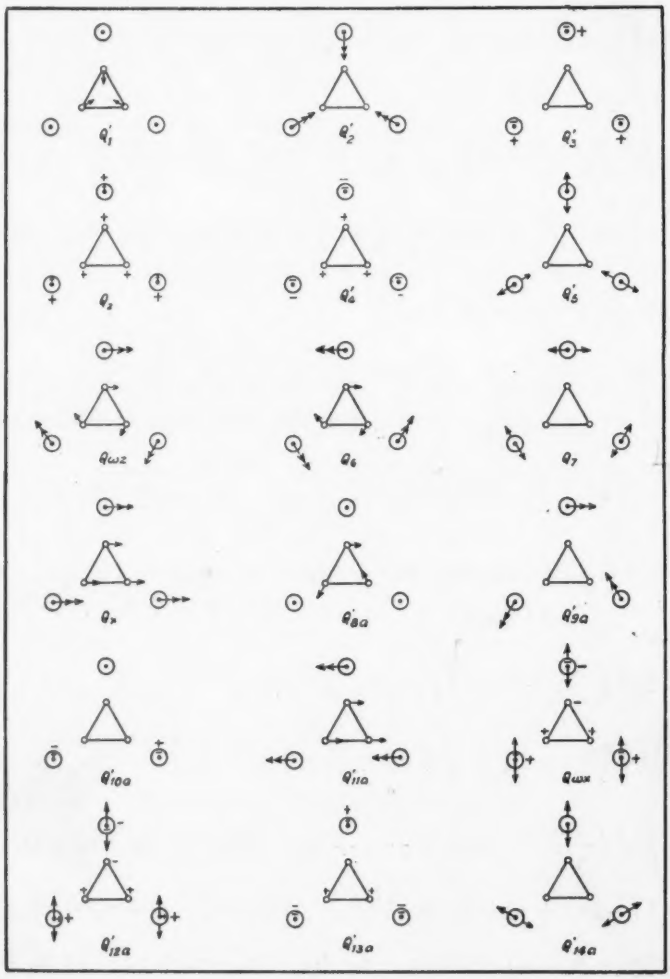


FIG. 2

5. *Potential Energy Function*

The potential function used for the calculation of frequencies contains seven force constants and is written as

$$2V = k_1 \Sigma (\Delta R)^2 + k_2 \Sigma (\Delta r)^2 + k_3 \Sigma (\Delta \psi)^2 + k_4 \Sigma (\Delta \Phi)^2 + k_5 \Sigma (\Delta \chi)^2 + k_6 \Sigma \Delta R \, \Delta \Phi + k_7 \Sigma \Delta R \, \Delta r ;$$

where ΔR and Δr are the variations in the lengths of the C–C and C–H bonds, $\Delta \psi$, $\Delta \Phi$, $\Delta \chi$ represent the variations of $\overset{C}{\diagdown}\!\!\diagup\overset{C}{}$ C–C, $\overset{C}{\diagdown}\overset{H}{}$ C–H, $\overset{C}{\diagup}\overset{H}{}$ C–H angles; k_1 and k_2 are the force constants of C–C and C–H valence; k_3, k_4 and k_5 are the $\overset{C}{\diagdown}\!\!\diagup\overset{C}{}$ C–C, $\overset{C}{\diagdown}\overset{H}{}$ C–H, and $\overset{C}{\diagup}\overset{H}{}$ C–H deformation force constants, k_6 and k_7 are the interaction terms involving the coupling of C–C valence with $\overset{H}{\diagdown}$ C–H deformation and C–H valence respectively. In the calculation of frequencies the terms k_3, k_4, k_5 have been replaced by k_3', k_4', k_5', where

$$k_3' = \frac{k_3}{4a^2}; \quad k_4' = \frac{k_4}{b^2}, \quad k_5' = \frac{k_5}{b^2}.$$

Manneback and Verleysen (1936) have indicated the necessity of using interaction constants in their calculation of the frequencies of ethylene molecule.

6. *Calculation of Frequencies*

The method of calculating frequencies is the same as followed by Bhagavantam and Venkatarayudu (1938).

In class A the frequencies are given by

$$\begin{vmatrix} (A - 3M\lambda^2) & -D & E \\ -D & (B - 6m\lambda^2) & -F \\ E & -F & (C - 6m\lambda^2) \end{vmatrix} = 0,$$

where $A = 9k_1 + 6k_2 \cos^2\phi + X \sin^2\phi + 12\sqrt{3}\, k_6 \sin\phi - 12\sqrt{3}\, k_7 \cos\phi$

$B = 6k_2 \cos^2\phi + X \sin^2\phi$

$C = 6k_2 \sin^2\phi + X \cos^2\phi$

$D = B + 6\sqrt{3}\, k_6 \sin\phi - 6\sqrt{3}\, k_7 \cos\phi$

$E = (6k_2 - X) \sin\phi \cos\phi - 6\sqrt{3}\, k_6 \cos\phi - 6\sqrt{3}\, k_7 \sin\phi$

$F = (6k_2 - X) \sin\phi \cos\phi$

$$X = 12k_4' + \frac{36\, k_5' \sin^2\phi}{4 - 3\cos^2\phi}.$$

Therefore $\lambda_1^2+\lambda_2^2+\lambda_3^2 = k_2\left(1+\frac{\cos^2\phi}{6}\right)+\frac{k_1}{4}+X'\left(1+\frac{\sin^2\phi}{6}\right)$

$$+\frac{k_6'}{6}\sin\phi-\frac{k_7'}{6}\cos\phi\,;$$

$$\Sigma\lambda_1^2\lambda_2^2=\frac{7}{6}k_2X'+\frac{k_1}{4}(k_2+X')+\frac{k_6'}{6}\left(k_2\sin\phi-\frac{k_6'}{4}\right)$$

$$-\frac{k_7'}{6}\left(X'\cos\phi+\frac{k_7'}{4}\right);$$

$$\lambda_1^2\lambda_2^2\lambda_3^2=\frac{k_2X'k_1}{4}-\frac{(k_6')^2k_2+X'(k_7')^2}{24};$$

where $k_6'=2\sqrt{3}\,k_6;\ k_7'=2\sqrt{3}\,k_7;\ X'=2k_4'+\frac{6k_5'\sin^2\phi}{4-3\cos^2\phi}$.

In class B the frequencies are given by

$$\lambda_4^2+\lambda_5^2=\frac{k_2}{m}\left(1+\frac{2m}{M}\sin^2\phi\right)+\frac{6k_5'\sin^2\phi}{m(4-3\cos^2\phi)}\left(1+\frac{2m}{M}\cos^2\phi\right);$$

$$\lambda_4^2\lambda_5^2=\frac{k_2}{m}\frac{k_5'}{m}\frac{6\sin^2\phi}{4-3\cos^2\phi}\frac{M+2m}{M}.$$

For class C $\lambda_6^2=\frac{k_5'}{4-3\cos^2\phi}\frac{3\left(\frac{2}{\sqrt{3}}+\frac{b}{a}\cos\phi\right)m+2M}{mM}$.

For class D $\lambda_7^2=\frac{2k_5'}{m(4-3\cos^2\phi)}$.

In class E_1 the frequencies are given by

$$\begin{vmatrix} (A-12M\lambda^2) & E & H & F \\ E & (B-24m\lambda^2) & I & G \\ H & I & (C-4m\lambda^2) & J \\ F & G & J & \left(D-\frac{24mM}{2m+M}\lambda^2\right) \end{vmatrix}=0$$

where $A=18k_1+12k_2\cos^2\phi+54k_3'+24k_4'\sin^2\phi$

$$+\frac{4k_5'}{4-3\cos^2\phi}\left\{4\left(1+\frac{\sqrt{3}}{4}\frac{b}{a}\cos\phi\right)^2\right.$$

$$\left.+\left(1+3\sin^2\phi-\frac{\sqrt{3}}{2}\frac{b}{a}\cos\phi\right)^2+\left(1-3\sin^2\phi+\sqrt{3}\frac{b}{a}\cos\phi\right)^2\right\}$$

$$+12\sqrt{3}\,(k_6\sin\phi-k_7\cos\phi)\,;$$

$$B=12k_2\cos^2\phi+24k_4'\sin^2\phi+\frac{4k_5'}{4-3\cos^2\phi}\{4+(1+3\sin^2\phi)^2$$

$$+(1-3\sin^2\phi)^2\}\,;$$

$$C = 4k_2 \sin^2\phi + 8k_4' \cos^2\phi + \frac{4k_5'}{4 - 3\cos^2\phi} \cdot 6 \sin^2\phi \cos^2\phi ;$$

$$D = B ;$$

$$E = -12k_2 \cos^2\phi - 24k_4' \sin^2\phi + \frac{4k_5'}{4 - 3\cos^2\phi} \times$$

$$\left\{-4\left(1 + \frac{\sqrt{3}}{4}\frac{b}{a}\cos\phi\right) - \left(1 + 3\sin^2\phi - \frac{\sqrt{3}}{2}\frac{b}{a}\cos\phi\right)(1 + 3\sin^2\phi)\right.$$

$$\left. - \left(1 - 3\sin^2\phi + \sqrt{3}\frac{b}{a}\cos\phi\right)(1 - 3\sin^2\phi)\right\}$$

$$- 6\sqrt{3}\{k_6 \sin\phi - k_7 \cos\phi\} ;$$

$$F = -12k_2 \cos^2\phi - 24k_4' \sin^2\phi + \frac{4k_5'}{4 - 3\cos^2\phi} \times$$

$$\left\{4\left(1 + \frac{\sqrt{3}}{4}\frac{b}{a}\cos\phi\right) + \left(1 + 3\sin^2\phi - \frac{\sqrt{3}}{2}\frac{b}{a}\cos\phi\right)(1 - 3\sin^2\phi)\right.$$

$$\left. + \left(1 - 3\sin^2\phi + \sqrt{3}\frac{b}{a}\cos\phi\right)(1 + 3\sin^2\phi)\right\}$$

$$- 6\sqrt{3}(k_6 \sin\phi - k_7 \cos\phi) ;$$

$$G = 12k_2 \cos^2\phi + 24k_4' \sin^2\phi + \frac{4k_5'}{4 - 3\cos^2\phi} \times$$

$$\{-4 - 2(1 + 3\sin^2\phi)(1 - 3\sin^2\phi)\} ;$$

$$H = 4\sqrt{3}k_2 \sin\phi\cos\phi - 8\sqrt{3}k_4' \sin\phi\cos\phi + \frac{4k_5'}{4 - 3\cos^2\phi} \times$$

$$\left\{-\left(1 + 3\sin^2\phi - \frac{\sqrt{3}}{2}\frac{b}{a}\cos\phi\right)\sqrt{3}\sin\phi\cos\phi\right.$$

$$\left. + \left(1 - 3\sin^2\phi + \sqrt{3}\frac{b}{a}\cos\phi\right)\sqrt{3}\sin\phi\cos\phi\right\} - 6(k_6\cos\phi + k_7\sin\phi) ;$$

$$I = -4\sqrt{3}k_2 \cos\phi\sin\phi + 8\sqrt{3}k_4' \sin\phi\cos\phi$$

$$+ \frac{4k_5'}{4 - 3\cos^2\phi}\sqrt{3}\sin\phi\cos\phi\{(1 + 3\sin^2\phi) - (1 - 3\sin^2\phi)\} ;$$

$$J = I.$$

The frequencies in class E_2 are given by the determinant

$$\begin{vmatrix} (A - G\lambda^2) & D & F \\ D & (B - H\lambda^2) & E \\ F & E & (C - I\lambda^2) \end{vmatrix} = 0$$

Where $A = (c + 2b \sin\phi)^2 \left\{ 12\, k_2 \cos^2\phi + \frac{48\, k_5' \sin^4\phi}{4 - 3\cos^2\phi} + \frac{48\, k_5'}{4 - 3\cos^2\phi} \times \left(1 - \frac{\cos^2\phi}{2}\right)^2 + \frac{48\, k_5'}{4 - 3\cos^2\phi} \frac{\cos^2\phi}{4} \right\}$;

$$B = 48\, k_2 s^2 \sin^2\phi + \frac{16\, k_5'}{4 - 3\cos^2\phi} \sin^2\phi \left\{ 2\sqrt{3} \cos\phi \cdot s + \frac{3b}{a} \frac{m^{\frac{1}{2}}}{M^{\frac{1}{2}}} \left(\frac{2a}{\sqrt{3}} + b \cos\phi \right) \right\}^2 + \frac{16\, k_5'}{4 - 3\cos^2\phi} \left\{ \frac{3m^{\frac{1}{2}}}{M^{\frac{1}{2}}} \left(\frac{2a}{\sqrt{3}} + b \cos\phi \right) \times \frac{b}{a} \sin\phi + \sqrt{3} \sin\phi \cos\phi \cdot s \right\}^2 + \frac{48\, k_5'}{4 - 3\cos^2\phi} s^2 \sin^2\phi \cos^2\phi ;$$

$$C = 12\, k_2 \cos^2\phi + \frac{48\, k_5'}{4 - 3\cos^2\phi} \sin^4\phi + \frac{48\, k_5'}{4 - 3\cos^2\phi} \frac{\cos^4\phi}{4} + \frac{48\, k_5'}{4 - 3\cos^2\phi} \left(1 - \frac{\cos^2\phi}{2}\right)^2 ;$$

$$D = (c + 2b \sin\phi) \Big[- 24 k_2\, s \sin\phi \cos\phi + \frac{48\, k_5'}{4 - 3\cos^2\phi} \sin^3\phi \times \left\{ 2s \cos\phi + \sqrt{3} \frac{b}{a} \frac{m^{\frac{1}{2}}}{M^{\frac{1}{2}}} \left(\frac{2a}{\sqrt{3}} + b \cos\phi \right) \right\} + \frac{48\, k_5'}{4 - 3\cos^2\phi} \times \sin\phi \left(1 - \frac{\cos^2\phi}{2}\right) \left\{ s \cos\phi + \sqrt{3} \frac{b}{a} \frac{m^{\frac{1}{2}}}{M^{\frac{1}{2}}} \left(\frac{2a}{\sqrt{3}} + b \cos\phi \right) \right\} - \frac{24\, k_5'}{4 - 3\cos^2\phi} \cos^3\phi \cdot \sin\phi \cdot s. \Big] ;$$

$$E = 24\, k_2 \sin\phi \cos\phi \cdot s - \frac{48\, k_5'}{4 - 3\cos^2\phi} \sin^3\phi \times \left\{ 2s \cos\phi + \sqrt{3} \frac{b}{a} \frac{m^{\frac{1}{2}}}{M^{\frac{1}{2}}} \left(\frac{2a}{\sqrt{3}} + b \cos\phi \right) \right\} + \frac{24\, k_5'}{4 - 3\cos^2\phi} \times \cos^2\phi \left\{ s \cos\phi + \sqrt{3} \frac{m^{\frac{1}{2}}}{M^{\frac{1}{2}}} \frac{b}{a} \left(\frac{2a}{\sqrt{3}} + b \cos\phi \right) \right\} \sin\phi - \frac{24\, k_5'}{4 - 3\cos^2\phi} (2 - \cos^2\phi)\, s \sin\phi \cos\phi ;$$

$$F = (c + 2b \sin\phi) \left\{ - 12 k_2 \cos^2\phi - \frac{48\, k_5'}{4 - 3\cos^2\phi} \sin^4\phi + \frac{24\, k_5'}{4 - 3\cos^2\phi} \cos^2\phi\, (2 - \cos^2\phi) \right\} ;$$

$$G = 32a^2 M + 24m c^2 + 48m\left(\frac{2a}{\sqrt{3}} + b\cos\phi\right)^2;$$

$$H = 24m\left(\frac{2a}{\sqrt{3}} + b\cos\phi\right)^2 + 16a^2M$$

$$I = 24m.$$

In these expressions $c = \dfrac{\left(\dfrac{2a}{\sqrt{3}} + b\cos\phi\right)^2 + \dfrac{M}{m}\dfrac{2a^2}{3}}{b\sin\phi}$

and $s = \dfrac{a}{\sqrt{3}}\dfrac{M^{\frac{1}{2}}}{m^{\frac{1}{2}}} + \dfrac{m^{\frac{1}{2}}}{M^{\frac{1}{2}}}\left(\dfrac{2a}{\sqrt{3}} + b\cos\phi\right)$.

The frequencies ω in wave-numbers, is given by $\omega = \dfrac{\lambda}{2\pi c}$

where c is the velocity of light, and λ is the value calculated from the expressions given before.

7. *Evaluation of Force-Constants*

The force constants k_2 and k_5' were first calculated from the frequencies assumed for class B.[11] Using these, the force constants k_1, k_4', k_6, k_7 were calculated with the help of frequencies assumed for class A. The rest of the frequencies in classes C, D, E_1 and E_2 were then calculated by the help of these force-constants. The calculations are shown for

$$R\,(C\text{–}C) = 1{\cdot}53\ \text{Å and } \overset{H}{\underset{H}{\diagdown}}C\text{–}H = 109°\text{–}28'$$

and $$R\,(C\text{–}C) = 1{\cdot}54\ \text{Å and } \overset{H}{\underset{H}{\diagdown}}C\text{–}H = 108°.$$

TABLE III

		Calculated		Observed		Force-constants	
		R = 1·53 H\C − H=109°–28′	R (C − C) = 1·54 H\C − H = 108°	Raman	Infra-red	R (C − C) = 1·53 A° H\C − H = 109° − 28′	R (C − C) = 1·54A H\C − H = 108°
A	1	(1187)	(1187)	1187	*f*	k_1 (C − C) = 4·06 × 10^5	k_1 (C − C) = 4·04 × 10^5
	2	(1487)	(1487)	1472, 1504	*f*	k_4' H\C − H = ·3474 × 10^5	k_4' H\C − H = ·3486 × 10^5
	3	(3017)	(3017)	3010, 3028	*f*	k_6 = − ·5496 × 10^5	k_6 = − ·5467 × 10^5
						k_7 = − ·2009 × 10^5	k_7 = − ·1525 × 10^5
B	4	(3049)	(3049)	*f*	3049	k_2(C − H) = 4·901 × 10^5	k_2(C − H) = 4·91 × 10^5
	5	(1041)	(1041)	*f*	1041	k_5' C\C − H = ·4535 × 10^5	k_5' C\C − H = ·455 × 10^5
C	6	803	809	*f*	*f*		
D	7	719	724	*f*	*f*		
E_1	8	415	403	[382]	[ ]		
	9	822	829	863	860		
	10	1535	1528	1435	1435	k_3' C\C − C = − ·923 × 10^5 dynes	
	11	2976	2985	[ ]	[ ]		
E_2	12	764	748	736	*f*		
	13	1259	1252	[ ]	*f*		
	14	3065	3065	3079	*f*		

The frequencies within brackets ( ) have been assumed for the purpose of calculating force-constants. Brackets [ ] indicate that the frequencies have either not been observed or the measurements are not definite on account of the very weak intensity of the lines.

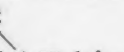
The agreement between the calculated and observed values is fairly good. The table explains all the observed frequencies satisfactorily. Only one line (1528) deviates from the observed value 1435 by about 6%. Other lines may be considered as overtones or combinations

$1454 \backsimeq 2 \times 724$	$1890 \backsimeq 1187 + 724$
$2852 \backsimeq 2 \times 1435$	$2083 \backsimeq 1187 + 860$
$2952 \backsimeq 2 \times 1472$	$2179 \backsimeq 1435 + 724$
$1739 \backsimeq 1041 + 724$	$2331 \backsimeq 1487 + 860$
$1779 \backsimeq 1434 + 382$	$2494 \backsimeq 1485 + 1041 ; 1252 + 1187$
	$2632 \backsimeq 1485 + 1187$

Barring the first three lines which are observed in the Raman spectrum all the rest are infra-red bands.

The values of C–C and C–H force-constants have been calculated as $4 \cdot 04$ and $4 \cdot 91 \times 10^5$ dynes. These values are quite in agreement with the usual values of these force-constants found in other compounds. Both the

C–H and



C–H deformations are positive and equal to $\cdot 3486$ and $\cdot 455 \times 10^5$

dynes respectively while the C–C deformation and the interaction constants k_6 and k_7 are negative. Manneback and Verleysen (1936) have also found negative interaction force-constants for the ethylene molecule. The negative

value of the C–C deformation is not surprising in view of the highly strained nature of the C–C bonds.

8. *Completely Plane Model Examined*

It is interesting to study from the point of view of molecular structure whether a completely plane model of cyclopropane (in which the hydrogens are in the same plane as carbons) is a possibility. The symmetry group for the model remains D_{3h} but the number of vibrations coming under various classes are altered. This is seen from the character Table IV given below.

TABLE IV

D_{3h}	E	$2S_3$	$2C_3$	$3C_2$	σ_h	$3\sigma_v$	No. and nature of internal vibrations					Selection rules		No. and nature of internal vibrations for the previous model			
												Raman	Infra-red				
A ..	1	1	1	1	1	1	ω_1		δ		ν	pol.	f	ω_1		δ	ν
B ..	1	−1	1	−1	−1	1		γ				f	a		γ		ν
C ..	1	1	1	−1	1	−1		γ			ν	f	f		γ		
D ..	1	−1	1	1	−1	−1		γ				f	f		γ		
E_1 ..	2	−1	−1	0	2	0	$\omega_{2,3}$	γ	δ_1	δ_2	ν	dep.	a	$\omega_{2,3}$	γ	δ	ν
E_2 ..	2	1	−1	0	−2	0		γ	δ			dep.	f		γ	δ	ν
u_R ..	9	0	0	1	9	1											
ϵ_R ..	21	0	0	3	9	3											

The nature of vibrations has been stated by considering the symmetry co-ordinates of the previous model and the plane model. The symmetry co-ordinates of the plane model are

$$Q_1' \rightarrow x_1 + x_2 + x_3 \quad \ldots \ldots \ldots \ldots \ldots \ldots$$
$$Q_2' \rightarrow x_4 + x_5 + x_6 + x_7 + x_8 + x_9 \quad \ldots \ldots \ldots \ldots \quad \text{A (3)}$$
$$Q_3' \rightarrow y_4 + y_5 + y_6 - y_7 - y_8 - y_9 \quad \ldots \ldots \ldots \ldots$$

$$Q_4 \rightarrow 2m^{\frac{1}{2}}(z_1 + z_2 + z_3) - M^{\frac{1}{2}}(z_4 + z_5 + z_6 + z_7 + z_8 + z_9) \quad \ldots \quad \text{B (1)}$$

$$Q_5' \rightarrow 2m^{\frac{1}{2}}(y_1 + y_2 + y_3) - M^{\frac{1}{2}}(y_4 + y_5 + y_6 + y_7 + y_8 + y_9) \quad \ldots$$
$$Q_6' \rightarrow x_4 + x_5 + x_6 - x_7 - x_8 - x_9 \quad \ldots \ldots \ldots \ldots \quad \text{C (2)}$$

$$Q_7 \rightarrow z_4 + z_5 + z_6 - z_7 - z_8 - z_9 \quad \ldots \ldots \ldots \ldots \quad \text{D (1)}$$

$$Q_x \rightarrow M^{\frac{1}{2}}\{(2y_1 - y_2 - y_3) - \sqrt{3}(x_2 - x_3)\} +$$
$$m^{\frac{1}{2}}\{x_4 \cos a + y_4 \sin a - x_5 \cos(a - 60) - y_5 \sin(a - 60)$$
$$+ x_6 \cos(120° - a) - y_6 \sin(120° - a) + x_7 \cos\beta + y_7 \sin\beta - x_8 \cos(\beta - 60)$$
$$- y_8 \sin(\beta - 60) + x_9 \cos(120° - \beta) - y_9 \sin(120° - \beta)\}$$

$$Q_{8a}' \rightarrow (2y_1 - y_2 - y_3) + \sqrt{3}(x_2 - x_3)$$

$$Q_{9a}' \rightarrow \{x_4 \cos\alpha + y_4 \sin\alpha - x_5 \cos(\alpha - 60) - y_5 \sin(\alpha - 60) + x_6 \cos(120° - \alpha) - y_6 \sin(120° - \alpha)\} - \{x_7 \cos\beta + y_7 \sin\beta - x_8 \cos(\beta - 60) - y_8 \sin(\beta - 60) + x_9 \cos(120° - \beta) - y_9 \sin(120° - \beta)\}$$

$$Q_{10a}' \rightarrow \{(2y_4 - y_5 - y_6) + \sqrt{3}(x_5 - x_6)\} + \{(2y_7 - y_8 - y_9) + \sqrt{3}(x_8 - x_9)\}$$

$$Q_{11a}' \rightarrow \{(2y_4 - y_5 - y_6) + \sqrt{3}(x_5 - x_6)\} - \{(2y_7 - y_8 - y_9) + \sqrt{3}(x_8 - x_9)\}$$

$$Q_{12a}' \rightarrow m^{\frac{1}{2}}\{(2y_1 - y_2 - y_3) - \sqrt{3}(x_2 - x_3)\} - 2M^{\frac{1}{2}}\{x_4 \cos\alpha + y_4 \sin\alpha - x_5 \cos(\alpha - 60) - y_5 \sin(\alpha - 60) + x_6 \cos(120° - \alpha) - y_6 \sin(120° - \alpha) + x_7 \cos\beta + y_7 \sin\beta - x_8 \cos(\beta - 60) - y_8 \sin(\beta - 60) + x_9 \cos(120° - \beta) - y_9 \sin(120° - \beta)\}$$

$E_1(5)$

$$Q_{wx} \rightarrow \left[M^{\frac{1}{2}} \frac{a}{\sqrt{3}}(-2z_1 + z_2 + z_3) + m^{\frac{1}{2}}\left\{\left(\frac{2a}{\sqrt{3}} + b\cos\phi\right)(-z_4 - z_7) + \left(\frac{a}{\sqrt{3}} - b\sin\overline{\phi - 30}\right)(z_6 + z_8) + \left(\frac{a}{\sqrt{3}} + b\sin\overline{\phi + 30}\right)(z_5 + z_9)\right\}\right]$$

$$Q_{13a}' \rightarrow m^{\frac{1}{2}}(2a^2 + \tfrac{3}{2}b^2 + 2\sqrt{3}\,ab\cos\phi)(-2z_1 + z_2 + z_3) - \sqrt{3}\,a\,M^{\frac{1}{2}}\left[\left(\frac{2a}{\sqrt{3}} + b\cos\phi\right)(-z_4 - z_7) + \left(\frac{a}{\sqrt{3}} - b\sin\overline{\phi - 30}\right)(z_6 + z_8) + \left(\frac{a}{\sqrt{3}} + b\sin\overline{\phi + 30}\right)(z_5 + z_9)\right]$$

$$Q_{14a}' \rightarrow b\sin\phi(z_4 + z_7) - \{a + b\cos(\phi - 30)\}(z_6 + z_8) + \{a + b\cos(\phi + 30)\}(z_5 + z_9).$$

$E_2(2)$

The above co-ordinates have been written for a model in which the hydrogen atoms 5 and 9 are below and hydrogen atoms 6 and 8 above the line joining carbon atoms 2 and 3. The hydrogen atom 4 is to the right and the hydrogen atom 7 to the left of the bisector passing through carbon atom 1. $(\alpha - 30°)$ and $(\beta - 30°)$ are the angles made by the lines $H_4 H_5$ and $H_7 H_8$ with the horizontal line parallel to $C_2 C_3$.

ω_1 and $\omega_{2,3}$ represent the ring vibrations, δ's are the C H_2 deformations and ν the (C–H) valence vibrations. γ represents the perpendicular CH_2 vibration and it is numerically very much lower than δ's and ν's. It is seen from the above table that for the plane model, class B contains only one vibration, *i.e.*, there should be only one infra-red absorption. This vibration

can only be a γ(C–H) frequency and therefore the strong infra-red absorption at 3049 should be forbidden. Similarly in class E_2 there are only two Raman active vibrations γ and δ for the plane model, therefore the strong Raman line at 3086 should also be forbidden. It is not likely that they belong to class E_1, because the symmetry co-ordinate corresponding to the line 3049 now goes to class C and is therefore forbidden in both infra-red and Raman effect. Therefore the Raman line 3080 and the infra-red absorption at 3049 cannot be explained on the completely plane model.

In conclusion, the author thanks Professor Sir C. V. Raman for his kind interest in the work.

9. *Summary*

Assuming that cyclopropane molecule has a structure in which the carbons form a regular triangle and the hydrogens lie at tetrahedral corners out of the plane of carbon ring (symmetry group D_{3h}) the normal modes of vibration and the force constants have been calculated. The results have been compared with the Raman and infra-red data of the molecule and fairly good agreement has been obtained. The frequencies can be assigned to six different classes of which two are doubly degenerate. Assuming the frequencies 3049 and 1041 as belonging to class B and 1187, 1487, 3017 as belonging to class A, the following force-constants have been calculated:

$$k_1\,(\mathrm{C\text{–}C}) = 4\cdot04 \times 10^5,\ k_2\,(\mathrm{C\text{–}H}) = 4\cdot91 \times 10^5,\ k_4'\,(\mathrm{C\text{–}H}) = \cdot3486 \times 10^5$$

$$k_5'\,(\mathrm{C\text{–}H}) = \cdot455 \times 10^5,\ k_6 = -\cdot5467 \times 10^5,\ k_7 = -\cdot1525 \times 10^5 \text{ dynes}$$

where k_1 and k_2 are the valence C–C and the valence C–H and k_4', k_5' are the deformation C–H, C–H, force-constants and k_6 and k_7 are the interaction terms involving a coupling of valence C–C with deformation C–H and valence C–H. The frequencies calculated for class E_2 are 748, 1252, 3065 (observed 736, [ ], 3079) and 809 for class C and 724 for class D. Taking $k_3'\,(\mathrm{C\text{–}C}) = -\cdot923 \times 10^5$ dynes the frequencies calculated for class E_1 are 403, 829, 1528, 2985 (observed [382], 860, 1435, [ ]).

The case for a completely plane model of cyclopropane (in which the hydrogens are in the same plane as carbons) has also been examined and it

has been shown that it does not explain the strong Raman line at 3086 and the strong infra-red absorption at 3049.

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PHOTOPOLYMERISATION OF ANTHRACENE IN BENZENE SOLUTION FROM THE MAGNETIC STANDPOINT

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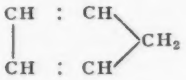
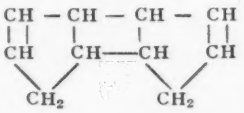
Received October 16, 1939

Farquharson[1] while investigating the magnetic behaviour of cyclopentadiene



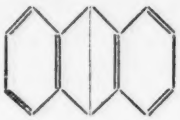
on polymerisation to dicyclo-pentadiene



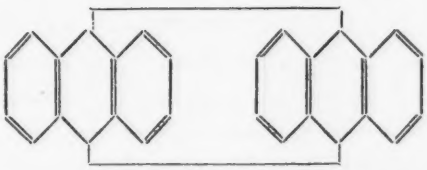
observed that as the polymerisation proceeded, the susceptibility value of the product decreased. Bhatnagar, Kapur and Hashmi[2] in their studies of the magnetic behaviour of photo-tropic substances observed that the susceptibility value of cinnamylidene-malonic acid on polymerisation to its dimer showed a decrease. A similar behaviour was observed in the case of thiophosgene on its polymerisation to its photodimer. In all these cases, the polymerised product is formed as a result of the disappearance of two double bonds, one from each of the parent molecules, and the formation of a bridged four-membered ring. As the polymerisation in such cases involves the change of $-C=C-$ double bonds to single bonds, therefore, according to Pascal's views there ought to be a rise in the diamagnetic susceptibility value of the polymerised product by $5{\cdot}5 \times 10^{-6}$ units. Bhatnagar, Kapur and Hashmi (*loc. cit*) suggested that the decrease rather than the increase of the susceptibility value of the polymerised products is probably due to the formation of a bridged ring. The exact value for λ the constitution correction factor for such a ring formation, cannot be deduced from the data already available, because in the case of cyclo-pentadiene the value of the dimer is not known and in the case of cinnamylidene malonic acid it is

difficult to get the pure polymerised product because of its tendency to oxidise easily.

It is well known that photopolymerisation of anthracene



to dianthracene



in solid state or in benzene solution leads to the disappearance of two double bonds, one from each of the molecules, and the formation of a bridged four-membered ring.[3] The present investigation was, therefore, undertaken in order to determine the value of λ, the constitution correction factor for the bridged four-membered ring, by a magnetic study of the products of this photo-polymerisation.

Experimental

Pure anthracene available in the stores was repeatedly crystallised from benzene till pure crystals with m.p. 213° C. were obtained. Particular care was taken to eliminate anthraquinone which, if present in small traces, has been observed to catalyse photochemical oxidation processes.[4] This was done by heating the hydrocarbon with zinc dust (Sudborough). Anthraquinone is, however, developed in the course of the reaction as has been shown in the sequel. The pure white crystals thus obtained were dissolved in pure thiophene-free benzene which had been kept over sodium wire for a fortnight and had been redistilled before use. The solution was exposed to sunlight in pyrex glass conical flasks and the magnetic susceptibility values of the product separating out from day to day were determined on a modified form of Gouy's magnetic balance.

It was observed that the anthracene solution remained colourless for the first two days and became pale yellow on the third day. It went on deepening in colour on further exposure till after a month it developed a deep orange red colour.

The susceptibility and the melting points of the solids which separated out at different intervals were determined and are tabulated below :—

Time of exposure days	Colour of insoluble product	M.p. of solid separating	$\chi \times 10^6$ of solid separating	Colour of the solution
		°C.		
0	(Pure anthracene) ..	213	− 0·728	..
1	Colourless	243–44	− 0·635	Colourless
2	Slightly coloured ..	241–42	− 0·593	Do.
3	Coloured	239–41	− 0·549	Pale yellow
4	Do.	236–39	− 0·546	Yellow
7	Light brown	232–55	− 0·532	Orange
30	Brown	180–85	− 0·286	Red

From the results given above, it is clear that the melting point and the susceptibility of the solid which separates out from day to day go on decreasing, indicating thereby that some other compounds besides dianthracene possessing a rather low magnetic susceptibility are also being formed.

Although the solid that separates out of the irradiated solution of anthracene in benzene after a week is brown, the compound that is crystallised out from this deep orange red solution is orange in colour and when further crystallised from pure acetone comes out as a needle-shaped buff coloured substance, having a susceptibility of $-0{\cdot}573 \times 10^{-6}$ and a m.p. of 280–82° C.

The analysis of the brown and the buff coloured compounds gave

	C	H	O
	%	%	%
Brown compound ..	81·40	4·85	13·75
Buff needle-shaped ..	80·80	4·00	15·20

(other elements such as nitrogen and sulphur were found to be absent).

It, therefore, appears that the change in colour of the solution is due to the formation of photo-oxidation products of anthracene. Chemical analysis and the physical constants of the buff coloured solid identify it as anthraquinone. (Anthraquinone gives C = 80·77, H = 3·85 and O = 15·38%.)

That the photo-oxidation products are responsible for the colour changes of the irradiated solution were further supported by the fact that when the

photopolymerisation of anthracene in a benzene solution was carried out in vacuum for a month, no such colour developed.

It was observed that dianthracene that separated out from solution of anthracene on exposure to light in vacuum was perfectly white with m.p. 244° C. and susceptibility -0.668×10^{-6}. For comparison the m.p. and the amounts of solid which separated out in vacuum and in contact with air are given below :—

Time days	M.p. of dianthracene		% of dianthracene formed	
	Vacuum	Air	Vacuum	Air
	°C.	°C.		
1	244	243–44	81·08	72·21
2	244	241–42	88·45	74·13
3	244	239–41	88·90	75·96
4	244	236–39	..	..
7	244	232–35	91·54	85·19

From the results it is clear that pure dianthracene is formed only in vacuum, whereas a mixture of compounds separates out in contact with air, and the amount of dianthracene formed in vacuum is more than that formed in air. The energy absorbed in both cases is the same, but whereas in vacuum the whole of this energy is used up in the formation of dianthracene in air it is partly utilized for the photo-oxidation of the hydrocarbon. Therefore, the amount of dianthracene formed in presence of air is less than that formed in vacuum.

If the fluorescent solution, after the removal of dianthracene formed when the exposure of anthracene solution in benzene was carried out in vacuum, is exposed to light in the presence of air, the solution becomes light red. The colour goes on deepening and a brown solid separates out.

This brown compound melts with decomposition at 180° C. and its composition is C, 69·00 ; H, 4·36 ; O, 26·64 %. Its susceptibility was found to be -0.212×10^{-6}. This analysis corresponds to $C_{14}H_{10}O_4$ (C, 69·42 ; H, 4·13 ; O, 26·45%).

The melting point and magnetic susceptibility of the brown compound separating out of the irradiated benzene solution from which dianthracene

has been removed in vacuum is different from that which is obtained from the irradiated benzene solution in air. In order to identify the latter compound and to see whether it was a pure or a mixed specimen, the brown material was shaken with acetone distilled over $KMnO_4$. It was noticed that a white insoluble compound (m.p. 243°) approximately 17·09% separated out and a brown soluble compound remained in solution (m.p. 180°). The brown compound had a susceptibility value $-0{\cdot}212 \times 10^{-6}$ which is the same as that of the brown compound, $C_{14}H_{10}O_4$, mentioned above. The melting point of the white compound corresponds to dianthracene. Moreover, if the susceptibility value of the original compound is calculated according to the mixture law, assuming it to be a mixture of dianthracene and the pure brown compound, it comes to be $-0{\cdot}290 \times 10^{-6}$, which is in very good agreement with its experimental susceptibility value of $-0{\cdot}286 \times 10^{-6}$.

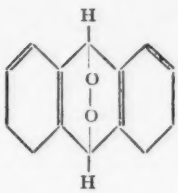
It was also observed that if pure dianthracene (m.p. 244° and $\chi = -0{\cdot}668 \times 10^{-6}$) separating out from anthracene solution irradiated in vacuum, is kept in benzene and exposed to light in the presence of air, the solution goes on changing its colour from day to day till it develops an orange red colour. The colour of dianthracene also goes on changing and becomes light brown after a fortnight. Its magnetic susceptibility was found to be $-0{\cdot}579 \times 10^{-6}$ which is much less than the value for pure dianthracene, $-0{\cdot}668 \times 10^{-6}$. This is clearly indicative of the formation of photo-oxidation products.

Discussion of Results

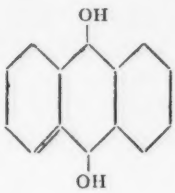
The photochemical change of anthracene to dianthracene has been investigated by numerous workers, and it has been regarded that anthracene is one of those substances which is most resistant to self-oxidation. Charles Dufraisse and Marcel Gerard[5] have, however, found that when a benzene solution of anthracene is irradiated in air, anthracene peroxide ($C_{14}H_{10}O_2$) is formed. The red benzene solution obtained by us after irradiation in air liberates iodine from KI in the presence of acetic acid. 0·0712 gm. of the solid in the deep orange red solution liberates iodine equivalent to 8·30 c.c. N/250 $Na_2S_2O_3$.

If the liberation of iodine from KI is due to anthracene peroxide only, then the amount of anthracene peroxide present in 0·0712 gm. of the solid in solution is only 4·897%.

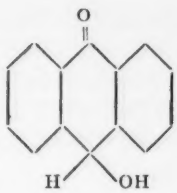
Anthracene peroxide is isomeric with anthrahydroquinone (I) and oxanthrone (II)[6]



(anthracene peroxide)



I



II

Anthrahydroquinone is brown coloured and melts at about 180° C., whereas oxanthrone is colourless and melts at 167° C. The brown compound that separates out of the irradiated solution melts with decomposition at 180° C. and has a composition corresponding to $C_{14}H_{10}O_4$, which has two oxygen atoms more than anthrahydroquinone. The mechanism of the formation of this compound can be pictured as follows: In the irradiated solution anthracene peroxide is formed first as suggested by Dufraisse and Gerard, which subsequently undergoes an isomeric change to anthrahydroquinone and ultimately an oxygenated derivative approximating to $C_{14}H_{10}O_4$ is formed although a part of the peroxide equivalent to 4·987% remains dissolved as such in the benzene solution. The oxygenated derivative is apparently anthrahydroquinone containing loosely bound oxygen.

Similar considerations apply to the development of the brown compound when a solution of dianthracene in benzene is irradiated in air. An equilibrium anthracene $\rightleftharpoons$ dianthracene is first established and this is followed by a slow photochemical oxidation of anthracene to its oxygenated derivatives.

The origin of anthraquinone in the solution phase is to be sought in the photochemical oxidation of anthrahydroquinone. The work of Gardner and Goldstein[7] on the photolysis of chloro-derivative of anthrahydroquinone in which they were able to show that anthrahydroquinone undergoes oxidation to anthraquinone in the presence of air, affords a fair confirmation of this view.

Determination of the value for λ.—It has been shown that when photopolymerisation of anthracene is carried out in air, besides dianthracene, other compounds with low susceptibility values are also formed, but if anthracene solution is exposed to light in vacuum, pure dianthracene alone is formed. Therefore, in order to determine the value for λ, the constitutive factor for a bridged four-membered ring formed as a result of the disappearance of double bonds during the course of polymerisation, the susceptibility value of pure dianthracene formed as a result of the exposure to sunlight of pure anthracene solution in evacuated flasks was determined on a Gouy's balance. Its susceptibility value was found to be $-0{\cdot}668 \times 10^{-6}$.

According to Pascal's well-known principle of the additivity of the diamagnetic properties of non-polar compounds the molecular susceptibility χ_M of a molecule can be closely represented as $\chi_M = \Sigma\chi_A + \lambda$, where $\Sigma\chi_A$ represents the sum of the atomic susceptibilities of all the atoms in the molecule and λ is the constitutive factor depending on the nature of linkages between the atoms.

When polymerisation takes place between two molecules of anthracene to form dianthracene the magnetic susceptibility of dianthracene will be given by an expression similar to that given by Pascal for the formation of molecules from atoms, *i.e.*,

$$\chi_M = 2\chi_A + \lambda,$$

where χ_M is the molecular susceptibility of dianthracene, χ_A susceptibility of anthracene, and λ the constitution factor arising from the new ring formed. The experimental molecular magnetic susceptibility value for dianthracene is equal to $-237\cdot80 \times 10^{-6}$ and that for anthracene is equal to $-129\cdot7 \times 10^{-6}$ ($-0\cdot7288 \times 178$)

$$\begin{aligned}\lambda &= \chi_M - 2\chi_A \\ &= -237\cdot8 + 2 \times 129\cdot7 \\ &= +21\cdot6.\end{aligned}$$

Farquharson and Sastri[8] determined the values of constitutive correction factor for polymethylene rings and obtained a value of $+3\cdot05 \times 10^{-6}$ for a four-membered ring. Our constitutive factor value for a four-membered ring formed as a result of the disappearance of two double bonds during the course of polymerisation is $21\cdot6 \times 10^{-6}$ which value is much higher than the one obtained by Farquharson and Sastri. They obtained the constitutive factor value for various polymethylene rings simply by comparing corresponding open-chain and cyclic compounds.

When the polymerisation of compounds such as that of anthracene to dianthracene takes place the following structural changes accompany it :

(1) The loss of two double bonds, one from each of the molecules.

(2) The formation of a four-membered ring.

(3) Change in the effective radius of the polymerised product.

(4) Influence of various groups on the valency angles of the ring formed.

From the magnetic standpoint the effect of change (1) would be to increase the diamagnetism of the polymerised product formed and the magnetic value for this change can be assessed because λ for $-C=C-$ is

known to be $5{\cdot}5 \times 10^{-6}$. If the value $3{\cdot}05 \times 10^{-6}$ for a four-membered ring obtained by Farquharson and Sastri (*loc. cit.*) be taken to account for the change, (2) and the effect due to the magnetic changes accompanying processes (3), and (4) be regarded negligible, the effect of polymerisation would be to increase the diamagnetism of the polymerised product. This is contrary to observations.

It is clear, therefore, that the influence of changes (3) and (4) on the magnetic property of the polymerised product cannot be ignored. It is very difficult to obtain an exact magnetic value for the changes (3) and (4).

The large fall in diamagnetism observed on polymerisation can be explained, however, by assuming that the polymerisation of two molecules of anthracene to one molecule of dianthracene is accompanied by a decrease in the radius of the polymerised molecule formed, and the influence of the benzene rings on the valency angles seems to lead to a concentration of the electronic charge in the rings leading to a smaller effective radius and both these factors would contribute to a large fall in diamagnetism.

From these considerations it is obvious that the value of λ, $21{\cdot}6 \times 10^{-6}$ will not be the same for all such cases of polymerisation but would be mainly influenced by the magnetic changes accompanying processes (3) and (4). Thus the value of λ when thiophosgene polymerises to its photodimer is $+ 11{\cdot}5 \times 10^{-6}$ (Bhatnagar, Kapur and Hashmi, *loc. cit.*).

As polymerisation of anthracene in benzene solution in vacuum proceeds, dianthracene is formed, part of it remains in solution in equilibrium with anthracene. The mass susceptibility χ of the complex in solution at any stage, according to Farquharson (*loc. cit.*) would be

$$\chi = \frac{n\chi_A + (n-1)\lambda}{n\,M_A},$$

where n = number of molecules of anthracene which polymerise

λ = polymerisation constitution constant

χ_A = molecular susceptibility of anthracene

M_A = molecular weight of anthracene.

In this expression λ, χ_A and M_A are constants and the curve for the change in the mass susceptibility with the number of simple molecules in the complex will be a hyperbola. Thus at any stage the mass susceptibility can be employed to calculate the composition of the mixture of the polymerised and unpolymerised molecules.

Time in hrs.	$\chi \times 10^{-6}$ of the mixture	% of anthracene in the mixture	
		Calculated from magnetic data	Determined by sublimation
1	0·7278	98·3	98·4
2	0·7273	97·0	97·2
3	0·7264	95·0	95·1
4	0·7254	93·4	93·2

In the second column of the table is given the mass susceptibility value of the solid obtained from time to time by evaporating benzene in vacuum from an anthracene solution exposed to light in vacuum. The third and the fourth columns give the percentage composition of the mixture as calculated from the magnetic data and as determined by subliming off anthracene from the known weight of the mixture, respectively.

It is clear from the table that the percentage composition of the mixture as determined by magnetic data agrees well with those obtained by the sublimation method.

The authors wish to thank Dr. K. S. Narang for doing the microanalysis of the compounds.

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DIFFRACTION OF LIGHT BY A THIN METALLIC HALF-PLANE

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Received November 28, 1939

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

The diffraction problem of the Fresnel class which has received the greatest amount of attention in the literature is that first considered by Fresnel himself, namely, the effect of an opaque obstacle bounded by a straight edge. When light passes by such an obstacle, the illumination on the brighter side of the pattern exhibits maxima and minima of intensity following one another which are, however, not very conspicuous and become even less so, as we recede from the boundary of the shadow, until they disappear, finally, in uniform illumination at a short distance from it. Within the geometric shadow, the illumination does not fall abruptly to zero at its edge, but fades off continuously but rapidly to very small values as we recede farther and farther from it. If, instead of an opaque obstacle, we have a very thin lamina bounded by a sharp edge, we observe maxima and minima of illumination of the kind described above on both sides of the pattern, instead of only on one side as in the case of the opaque screen. The shadow of the edge of the lamina is a minimum of illumination and the bands following it are symmetrically disposed on either side. This effect is explained as due to the difference in the phase of the part of the wave-front which has passed through the lamina relatively to the other part, the difference of amplitudes which arises at the same time being relatively less important. In the present paper, we shall consider the effect on the propagation of light of a thin metallic lamina bounded by a straight edge. C. F. Meyer (1934) has made a brief mention of this case, but has not considered it in any detail. Since a metallic lamina can only be partially transparent, the part of the wave-front transmitted through it undergoes not only a change of phase but also a notable diminution in amplitude relatively to the part that passes by the edge without interruption. One might perhaps, therefore, expect that the diffraction pattern in this case would exhibit features intermediate between those observed with opaque and transparent screens. Actually, the observations made by the present author show that the diffraction patterns exhibit novel

features which are not noticed in the case of either the opaque or the transparent screen. An account is given of these features and an attempt is made to explain them theoretically. The problem of large-angle diffraction by thin metallic edges is not considered in the present paper and will form the subject of a later communication.

2. *Experimental Methods*

Preparation of the Metallic Edges.—The metallic screens used in the present investigation were prepared by evaporating the metal in a high vacuum and depositing it as a thin film bounded by a sharp straight edge, on a carefully cleaned microscope slide of glass, $3'' \times 1''$ in size. For this purpose, the slide was mounted in the vacuum chamber, at a suitable height above the heating filament which consisted of a uniform coil of No. 30 S.W.G. tungsten wire loaded at intervals with sufficiently tiny V-shaped riders made out of fine silver wire of 0·3 mm. diameter. With this arrangement, films of uniform thickness could be obtained. To have the film terminating in a sharp edge, a new safety-razor blade with a suitable baffle was adjusted at the correct angle between the slide and the filament, so that the edge of the blade came into good contact with the surface of the glass slide without any intervening gaps (Fig. 1). This allowed the deposition to take place only on the portion of the glass left unmasked, leaving the other portion perfectly free from any deposit whatever. Special care was taken as not to scratch the glass with the edge of the blade while adjusting it prior to deposition, and also as not to spoil the edge of the film while removing the glass from the stand after deposition. Films of any desired thickness could be prepared. The thinnest of the films used in the present study, was light brown in colour and the thickest almost opaque. Films of intermediate thickness ranged in colour from light blue to dark violet when viewed by transmitted light. An examination of these films under the microscope revealed that the edges were sharp and straight.

Photographing the Patterns.—Visual examination of the patterns was made with white light. For photographing them, approximately monochromatic light (width of band 75–100 A.U.) got by limiting the continuous spectrum of a 500 c.p. tungsten pointolite lamp, by an adjustable vertical slit, was made use of. This was found to be preferable to using a mercury arc lamp, since the interference bands due to the glass plate carrying the silver film became very prominent with highly monochromatic light and disturbed the diffraction effects now under study.

The diffraction camera consisted essentially of a long light-tight box (3–4 metres long) blackened on the inside and placed at about three metres

from the slit. The silver film was mounted with its plane vertical at one end of the box and could be tilted in its own plane by means of a suitable lever

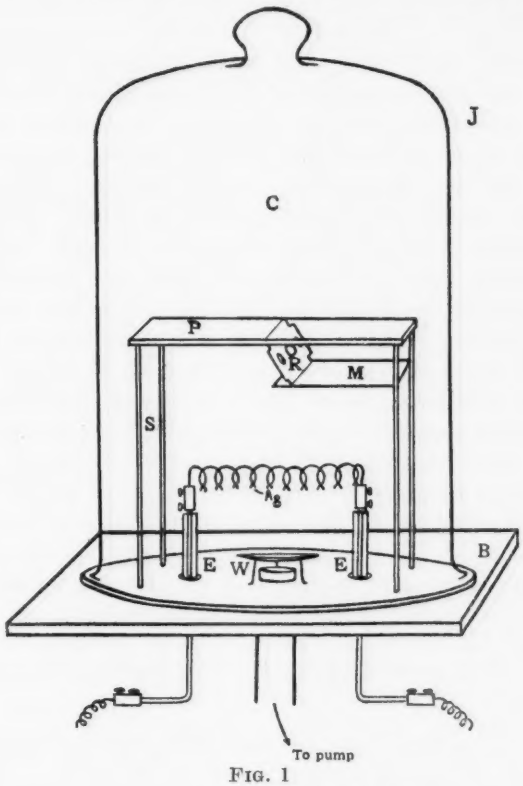

FIG. 1

J—Bell jar
P—Microscope slide
R—Safety-razor blade (Holder and tilting device not shown)
F—Heating filament of tungsten
W—Watch glass on small tripod to prevent stray bits of molten silver from falling into the pump.
C—Vacuum chamber
S—Stand
M—Baffle or mask
E, E—Insulated electrodes
Ag—Silver riders
B—Base plate

mechanism from the other end until the pattern as there seen showed the maximum definition.

3. *Description of the Pattern*

The nature of the diffraction bands on both sides of the pattern due to a metallic film with a sharp edge is found to depend upon the thickness of

the film and the wave-length of the light used, these two factors together determining the transparency of the film. With a moderately thick screen and using white light for visual illumination, a very striking difference is noticed between the fringes seen on the two sides of the pattern. The side of the pattern on which the light is enfeebled by passage through the film shows a very dark first minimum and lively alternations of colours following it, whereas on the other side of the pattern the alternations of intensity and colour are relatively quite inconspicuous, though the illumination is much more intense. Using approximately monochromatic light, the great difference between the two sides becomes more striking. On the less intense side of the pattern many more fringes are seen and their " visibility " is far greater than on the bright side. These features are exhibited in the photographs reproduced in Plates XIX and XX. All photographs except Plate XX, Fig. 4, were taken in red light. Plate XX, Fig. 4, was taken with violet light. Plate XIX, Fig. 1, shows the pattern on both sides for a fairly thin film. On account of the great difference in intensity of the two sides of the patterns when thick films are used, it becomes rather difficult with such films to secure photographs which exhibit both sides of the pattern in a satisfactory manner. In such a case it is advantageous to place a photometric wedge having a suitable gradient of transparency just in front of the photographic plate. Plate XIX, Fig. 2, shows a wedge photograph of the diffraction by a fairly thick film. The large number of fringes of high visibility are seen at the bottom of the left half of the figure and the feeble fringes on the bright side are seen at the top of the right half. The photograph also shows at the same time the relative intensities of both the sides and of the fringes on each side.

Figs. 1, 2 and 3 in Plate XX serve to show the changes taking place on the less intense side of the pattern with increasing thickness of the film. (The fluctuations of intensity on the brighter side of the pattern are not recorded owing to over-exposure.) In Fig. 1, which is the pattern for a film of medium thickness, the first minimum shows the best contrast. Fig. 2 corresponds to a thicker film. The first minimum has shifted away from the edge and the succeeding fringes too have moved away to a less extent. The pattern on the whole appears more crowded. The second minimum shows the best visibility. In Fig. 3, which is for a very thick film appearing dark violet by transmitted light—the thickness of this film roughly estimated was about 10^{-5} cm.—the shift of the fringes and the crowding of the lines are clearly seen. The first minimum is so feeble that it is barely distinguishable from the background. The visibility of the dark fringes increases up to the fifth fringe for which it is a maximum.

Fig. 4 shows the change in the pattern due to using violet light instead of red, the film used being the same as that for Fig. 3. The first dark band has shifted back towards the edge of the shadow and is much darker, while the minimum which has the best visibility is the second and not the fifth. The use of violet light instead of red has thus much the same effect as a reduction of the thickness of the film.

4. *Theory*

In the foregoing, we have been considering only the Fresnel pattern in transmission. In the region of reflection, a diffraction pattern can be seen which is roughly complementary to that observed in transmission. The reflection pattern can only be fully explained by taking into consideration the presence of the glass on which the silver film is deposited. At the moment, however, we are only concerned with the transmission patterns and we may, without serious error, ignore the glass plate and deal with the problem as if the metallic film were unsupported. The diffraction problem can be handled in an elementary fashion by writing down the Fresnel integrals, respectively, over the part of the wave-front which passes unobstructed and over the part which passes through the lamina with altered amplitude and phase and adding them up. Since however, it is possible to treat the problem rigorously on the basis of the electromagnetic theory, we shall do so and then deduce therefrom, the approximate expressions for the intensity in terms of Fresnel's integrals.

The wave equation in cylindrical co-ordinates is given by

$$\frac{\partial^2 u}{\partial \rho^2} + \frac{1}{\rho} \cdot \frac{\partial u}{\partial \rho} + \frac{1}{\rho^2} \cdot \frac{\partial^2 u}{\partial \phi^2} + \frac{\partial^2 u}{\partial z^2} - \frac{1}{c^2} \cdot \frac{\partial^2 u}{\partial t^2} = 0.$$

The exact solution of the wave equation in cylindrical co-ordinates for the case of an infinitely thin and perfectly reflecting semi-infinite screen bounded by a straight edge lying in the x-z plane with its edge parallel to the z-axis was first given by Sommerfeld (1896), from considerations based on the electromagnetic theory of light. The solution is given by

$$u = \mathrm{F}(\rho, \phi, \phi_0) \mp \mathrm{F}(\rho, \phi, -\phi_0),$$

where ϕ_0 is the angle which the plane of incidence makes with the plane of the lamina, the $\mp$ appearing according as the planes of incidence and polarisation are parallel or perpendicular to each other. In the $\|l$ case u represents the electric vector vibrating parallel to the edge and in the $_{\perp}r$ case the magnetic vector vibrating parallel to the edge. $\mathrm{F}(\rho, \phi, \phi_0)$ is of the form :

$$F(\rho, \phi, \phi_0) = e^{\frac{i2\pi t}{T}} \cdot \left(\frac{i}{\pi}\right)^{\frac{1}{2}} \cdot e^{ik\rho \cos(\phi - \phi_0)} \int_{-\infty}^{\tau} e^{-i\tau^2} \, d\tau,$$

where $$\tau = \sqrt{2k\rho} \cdot \cos \frac{\phi - \phi_0}{2}, \qquad (1)$$

and $F(\rho, \phi, -\phi_0)$ is got by writing $-\phi_0$ in place of ϕ_0 in the above expression.

The solution of Sommerfeld, however, is applicable only to an ideal screen which is not only infinitely thin but also perfectly reflecting at the same time. Such a screen is not met with in practice. A metallic film which is only a fraction of a wave-length thick $\left(\text{say}, \frac{\lambda}{5}\right)$ is almost opaque and approximates to an ideal semi-infinite screen. But even with such a film of a metal like silver or gold (metals with very high reflecting power), cent per cent reflection is never obtained. These considerations led Raman and Krishnan (1927) to modify the Sommerfeld theory in order to make it applicable to the case of actual opaque metallic screens. In their treatment of the problem, they took into account the actual reflecting power of the material of the screen and got the following solutions:

$$u_{\parallel} = F(\rho, \phi, \phi_0) - (A_s + i B_s) \cdot F(\rho, \phi, -\phi_0)$$
$$u_{\perp} = F(\rho, \phi, \phi_0) + (A_p + i B_p) \cdot F(\rho, \phi, -\phi_0), \qquad .. \quad (2)$$

where the quantities $(A_s + iB_s)$ and $(A_p + iB_p)$ represent the complex amplitudes of the perpendicular and the parallel components of the light reflected by the screen and depend only on the angle of incidence and the nature of the material of the screen.

That this comparatively simple modification of the Sommerfeld theory is sufficient to represent, in a very satisfactory manner, the behaviour of actual screens, has been recently confirmed by the experiments of Savornin (1939) with thin metallic wedges obtained by the method of cathodic sputtering. The ideas underlying the Raman-Krishnan theory were extended by Raman and Rao (1927) to enable the case of a thin transparent lamina to be dealt with. Here, the region corresponding to that of shadow when we consider an opaque screen, becomes that of transmission. By taking into account the transmission factor of the material of the lamina, they have derived the following solutions of the wave-equation in this particular case:

$$u_{\parallel} = F(\rho, \phi, \phi_0) - (A_s + iB_s) \cdot F(\rho, \phi, -\phi_0) + (C_s + iD_s) \cdot F(\rho, \phi, \phi_0 - 2\pi)$$
$$u_{\perp} = F(\rho, \phi, \phi_0) + (A_p + iB_p) \cdot F(\rho, \phi, -\phi_0) + (C_p + iD_p) \cdot F(\rho, \phi, \phi_0 - 2\pi), \qquad (3)$$

where $(C_s + iD_s)$ and $(C_p + iD_p)$ are the complex amplitudes of the components of the transmitted light and are, like the factors $(A_s + iB_s)$ and $(A_p + iB_p)$, dependent only on the angle of incidence for a particular screen.

The above expressions are quite general in their nature and apply to any transparent screen which is sufficiently thin, provided the terms $(A + iB)$ and $(C + iD)$ which depend on the material of the screen and the angle of incidence, are properly chosen. The Raman-Rao solutions of the wave-equation for a transparent lamina become entirely appropriate for the case of a thin metallic half-plane, by merely assigning proper values for the amplitudes of the reflected and transmitted radiations. By substituting the values of F (ρ, ϕ, ϕ_0), etc., in the equations (3), the expressions for the thin metallic lamina can be written down as

$$u_{\parallel} = e^{\frac{i2\pi t}{T}} \cdot \left(\frac{i}{\pi}\right)^{\frac{1}{2}} \left[e^{ik\rho \cdot \cos(\phi - \phi_0)} \int_{-\infty}^{\tau_1} e^{-i\tau^2}\, d\tau \right.$$

$$- (A_s + iB_s)\, e^{ik\rho \cos(\phi + \phi_0)} \int_{-\infty}^{\tau_2} e^{-i\tau^2}\, d\tau$$

$$\left. + (C_s + iD_s)\, e^{ik\rho \cos(\phi - \phi_0)} \int_{-\infty}^{\tau_3} e^{-i\tau^2}\, d\tau \right],$$

$$u_{\perp} = e^{\frac{i2\pi t}{T}} \left(\frac{i}{\pi}\right)^{\frac{1}{2}} \left[e^{ik\rho \cos(\phi - \phi_0)} \int_{-\infty}^{\tau_1} e^{-i\tau^2}\, d\tau \right.$$

$$+ (A_p + iB_p)\, e^{ik\rho \cos(\phi + \phi_0)} \int_{-\infty}^{\tau_2} e^{-i\tau^2}\, d\tau$$

$$\left. + (C_p + iD_p) \cdot e^{ik\rho \cos(\phi - \phi_0)} \int_{-\infty}^{\tau_3} e^{-i\tau^2}\, d\tau \right], \qquad \ldots \quad (4)$$

where τ_1, τ_2 and τ_3 are got by substituting ϕ_0, $-\phi_0$ and $\phi_0 - 2\pi$, respectively, for ϕ_0 in the value for τ given in (1).

In order to get at an expression for the Fresnel pattern we proceed in the following manner: For the usual case of Fresnel diffraction, we put $\phi_0 = \frac{\pi}{2}$ (*i.e.*, normal incidence) and take only the region close to the boundary of the geometric shadow on either side of it, *i.e.*, ϕ varies from the mean value of $\pi + \phi_0$ only by very small angles, and further, we consider ρ as large when compared with λ. Then the term due to reflection becomes negligibly

small and does not come into the calculation and since, for normal incidence, $C_s + iD_s = C_p + iD_p = C + iD$,

$$u_{\parallel} = u_{\perp} = e^{\frac{i2\pi t}{T}} \cdot \left(\frac{i}{\pi}\right)^{\frac{1}{2}} \cdot e^{ik\rho \cos(\phi - \phi_0)} \Big[\int_{-\infty}^{\tau_1} e^{-i\tau^2} d\tau + (C + iD) \int_{-\infty}^{-\tau_1} e^{-i\tau^2} d\tau \Big],$$

which can be written down in the familiar form of the Fresnel integrals, as:

$$u = e^{\frac{i2\pi t}{T}} \cdot e^{ik\rho \cos(\phi - \phi_0)} \left(\frac{1+i}{2}\right) \cdot \Big[\int_{-\infty}^{v_1} e^{-\frac{i\pi v^2}{2}} dv + (C + iD) \int_{-\infty}^{-v_1} e^{-\frac{i\pi v^2}{2}} dv \Big],$$

where $$v_1 = 2\sqrt{\frac{k\rho}{\pi}} \cdot \cos \frac{\phi - \phi_0}{2}.$$

The amplitude factor for the Fresnel pattern is given by

$$\left(\frac{1+i}{2}\right) \Big[\int_{-\infty}^{v_1} e^{-\frac{i\pi v^2}{2}} dv + (C + iD) \int_{-\infty}^{-v_1} e^{-\frac{i\pi v^2}{2}} dv \Big] \quad \ldots\ldots \quad (5)$$

i.e., as the sum of two Fresnel integrals, the first one taking into account the directly incident light and the second the light that is transmitted through the film. It is easily seen that when the film is opaque $(C + iD) = 0$ and thus the expression reduces to the usual Fresnel integral for an opaque screen.

The intensity of the pattern is given by

$$I = \tfrac{1}{2} \left| \int_{-\infty}^{v_1} e^{-\frac{i\pi v^2}{2}} dv + (C + iD) \int_{-\infty}^{-v_1} e^{-\frac{i\pi v^2}{2}} dv \right|^2.$$

By expanding the integrals into the sine and cosine terms and grouping suitably, the value of I can be shown to be

$$I = \tfrac{1}{2} [\{(1 - C) \cdot C(v_1) + \tfrac{1}{2}(1 + C + D) - D \cdot S(v_1)\}^2 + \{(1 - C) \cdot S(v_1) + \tfrac{1}{2}(1 + C - D) + D \cdot C(v_1)\}^2] \quad \ldots\ldots \quad (6)$$

The coefficients of reflection and transmission $(A + iB)$ and $(C + iD)$ for a metallic film can easily be calculated. Multiple reflections occur within the metallic film, although, due to the high absorption within the metal, the number of such internal reflections is very small. Following the method of Drude (1929) expressions for these coefficients for a metallic film can be derived; it can readily be shown that the relations obtained by Drude for these factors for normal incidence for a transparent plate taking into account all multiple reflections within the plate, also hold good for a metallic film,

provided the di-electric constant and quantities involving it be considered as complex. The Drude-expressions for the reflection and transmission coefficients at normal incidence for a metallic film can thus be shown to be

$$A + iB = \frac{i(\mu_2^2 - 1)\sin m}{i(\mu_2^2 + 1)\sin m + 2\mu_2 \cos m} \quad \ldots\ldots \quad (7)$$

$$C + iD = \frac{2\mu_2}{i(\mu_2^2 + 1)\sin m + 2\mu_2 \cos m} \quad \ldots\ldots \quad (8)$$

where both μ_2 and m are complex, given by $\mu_2 = \mu(1 - ik)$ and $m = \frac{2\pi\mu d}{\lambda}(1 - ik)$, μ, k being the optical constants of the metal for the particular wavelength λ of the incident light and d being the thickness of the film.

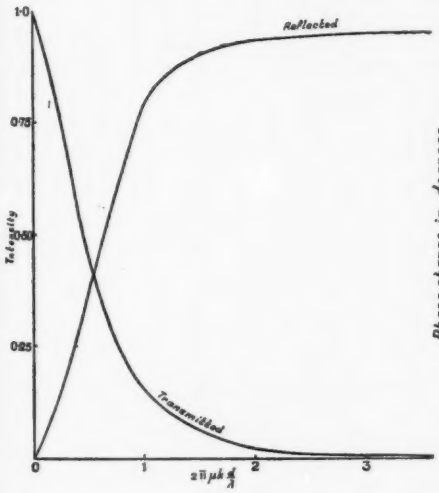

FIG. 2

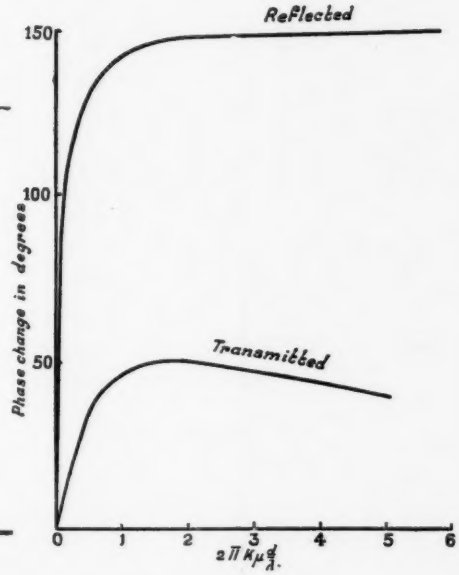

FIG. 3

The curves in Figs. 2 and 3 show the intensities and phases of the reflected and transmitted lights for silver films of different thicknesses calculated from the above formulæ, using the usual values of μ and k for silver for yellow light. The curves agree very well with those obtained by MacLaurin (1908) in his theory of Newton's rings by metallic reflection. The intensity of the reflected light at first increases very rapidly with increasing thickness and finally attains more or less a steady value. The

transmitted light falls off very rapidly in intensity at the beginning and with further increase of thickness diminishes gradually and becomes vanishingly small. The phases for both increase rapidly at first ; the phase for the reflected light attains a steady value, while, that for the transmitted light reaches a maximum value and then begins to diminish. It must be remembered, however, that when the phase has begun to diminish, the thickness of the film is such that it is almost opaque.

5. *Numerical Results from Theory*

The intensity curves computed for four different silver films of thicknesses $0 \cdot 54 \times 10^{-6}$ cm., $2 \cdot 7 \times 10^{-6}$ cm., $5 \cdot 4 \times 10^{-6}$ cm., and $8 \cdot 1 \times 10^{-6}$ cm., respectively, are shown in Figs. 4, 5, 6 and 7. The following features are noticed from the curves.

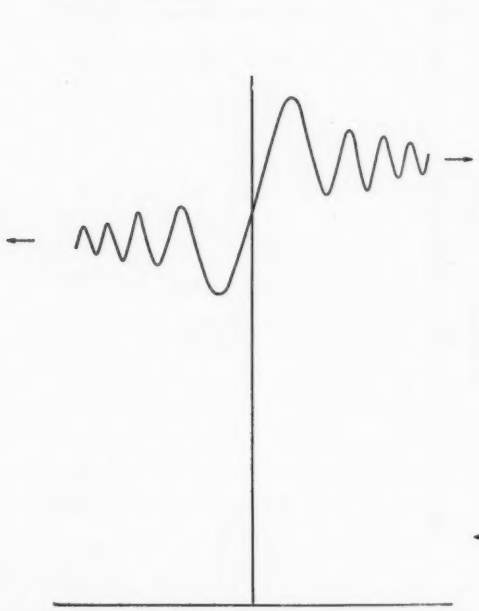

FIG. 4

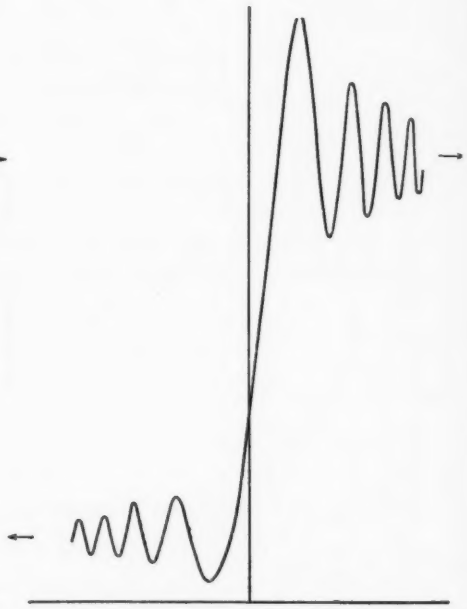

FIG. 5

With very thin films (Fig. 4) the fringe-systems on the two sides of the pattern are roughly similar, but the pattern is, however, far from being symmetrical. The fringes on the bright side are not very conspicuous and though they at first show a slight improvement in their appearance with

increasing thickness of the film, the further changes in them are not appreciable. The intensity at a sufficient distance from the edge is uniform and in all cases equals the intensity of the incident light. On the less intense side of the pattern, we observe that with increasing thickness of the film, the intensity falls off very rapidly, but that the visibility of the fringes, *i.e.*, the contrast between the maxima and minima increases. The first few maxima and minima of illumination shift away from the edge and approach closer to each other at the same time. This shift is largest for the first minimum. Only in the case of the thinner films is the first minimum the darkest. With increasing thickness, the first, second, third, fourth minima successively become the darkest. In Fig. 6, the second minimum on the less intense side

FIG. 6

FIG. 7

is the darkest whereas in Fig. 7, the fourth minimum is the darkest. At a sufficient distance from the edge, the intensity is uniform having a value equal to that of the intensity of the transmitted light. Table I shows the positions and intensities of the maxima and minima for the four films as got from the curves.

TABLE I

Thickness of film	Order of fringe	Dark side				Bright side			
		Maxima		Minima		Maxima		Minima	
		Position $-v_1$	2 × Intensity 2 I	Position $-v_1$	2 × Intensity 2 I	Position v_1	2 × Intensity 2 I	Position v_1	2 × Intensity 2 I
0.54×10^{-6} cm.	1	1·60	1·780	0·75	1·490	0·92	2·270	1·68	1·840
	2	2·55	1·755	2·14	1·520	2·20	2·125	2·62	1·865
	3	3·25	1·705	2·94	1·550	2·98	2·095	3·30	1·915
	4	3·83	1·695	3·55	1·565	3·57	2·070	3·81	1·935
2.7×10^{-6} cm.	1	1·62	0·480	0·90	0·090	1·12	2·620	1·80	1·640
	2	2·58	0·460	2·18	0·180	2·30	2·320	2·70	1·730
	3	3·26	0·390	2·97	0·210	3·05	2·230	3·35	1·810
	4	3·85	0·370	3·58	0·220	3·65	2·170	3·87	1·830
5.4×10^{-6} cm.	1	1·65	0·138	1·03	0·004	1·18	2·692	1·86	1·590
	2	2·62	0·122	2·21	0·003	2·35	2·362	2·74	1·715
	3	3·30	0·080	2·98	0·010	3·07	2·273	3·40	1·770
	4	3·86	0·070	3·61	0·013	3·68	2·222	3·95	1·805
8.1×10^{-6} cm.	1	1·65	0·065	1·18	0·0350	1·25	2·720	1·86	1·580
	2	2·62	0·060	2·24	0·0050	2·35	2·375	2·74	1·710
	3	3·30	0·030	3·00	0·0010	3·08	2·280	3·40	1·770
	4	3·87	0·025	3·61	0·0002	3·70	2·230	3·96	1·805
	5	4·35	0·020	4·12	0·0003				

6. *Discussion of the Data*

As is well known, the features observed in the diffraction of light by a semi-infinite screen bounded by a sharp edge are readily interpreted by considering the effects of the plane wave incident on the screen and of the diffracted cylindrical wave diverging from the edge; the latter diminishes

rapidly in amplitude as we proceed away from the edge. Within the geometric shadow, only the cylindrical wave appears, thus giving rise to a continuous but rapid fall of illumination in that region. On the brighter side the interferences between the parent plane wave and the comparatively weak cylindrical wave result in a few rather inconspicuous maxima and minima near the edge, and uniform illumination at a sufficient distance from it. The pattern observed with a thin metallic lamina can be explained in the same manner. On the bright side, the position is much the same except when very thin films are considered. On the feebler side of the pattern, maxima and minima arise due to the interference between the transmitted plane wave and the inflected cylindrical wave. The large number of bands on this side of the pattern and their comparatively high visibility are explained by the fact that the amplitude of the cylindrical wave is throughout comparable with that of the transmitted wave. For thin films the first minimum is the most conspicuous, because the intensity of the cylindrical wave even very near the edge is less than that of the transmitted wave and goes on diminishing as we recede from the edge. For thick films, the intensity of the cylindrical wave near the edge is actually greater than that of the transmitted plane wave. It diminishes and becomes equal to the latter at a distance from the edge and afterwards becomes smaller. This explains why the minimum with the best visibility, which occurs at the place where both the waves destroy each other completely or almost completely, marches into the "shadow" with increasing thickness of the film. The exact positions of the maxima and the minima of illumination depend both on the amplitudes and the phases of the interfering waves. Hence, while the way of looking at the matter indicated above, enables us to understand the general nature of the phenomenon, it does not permit of a simple calculation of the exact positions of the maxima and minima, especially near the edge. This can be done, however, by detailed calculation.

We have seen that for silver films, the use of violet light for illumination has the same effect on the patterns as that of diminishing the thickness of the films. This is because the region of selective transmission for silver lies in the violet. Metallic films of gold or copper, which also show marked selectivity, must behave similarly. The case of oblique incidence is also worthy of study and it is proposed to extend the investigations along these lines. Slits and other forms of aperture in metal films must also show diffraction patterns dependent on the thickness of the film as in the present case. In this connection it may be mentioned that some experimental work with fine slits ruled on absorbing films has been done by Pfund (1934) while studying anomalous dispersion by diffraction.

In conclusion, the author desires to express his grateful thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for suggesting the problem and for his kind guidance and encouragement during the course of the work.

7. *Summary*

A method has been devised for preparing uniform metallic films having edges of razor-like sharpness. Some novel features, which are not seen either in the case of an opaque screen bounded by a straight edge or in that of a transparent lamina, are observed in the Fresnel diffraction patterns with such silver films, the chief feature being the large number of fringes with high visibility to be found on the darker side of the pattern. The changes taking place with increasing thickness of the film and also with the wavelength of the incident light are described. It has been found that the minimum having the best visibility marches into the "shadow" to a fringe of higher order as the thickness of the film is increased.

The problem has been treated theoretically and intensity curves for the patterns for four films of different thicknesses have been drawn. The results are in agreement with experiment. By considering the interferences between the incident or the transmitted plane wave and the diffracted cylindrical wave diverging from the edge, the general features of the phenomenon can be readily interpreted in much the same way as in the case of an opaque screen.

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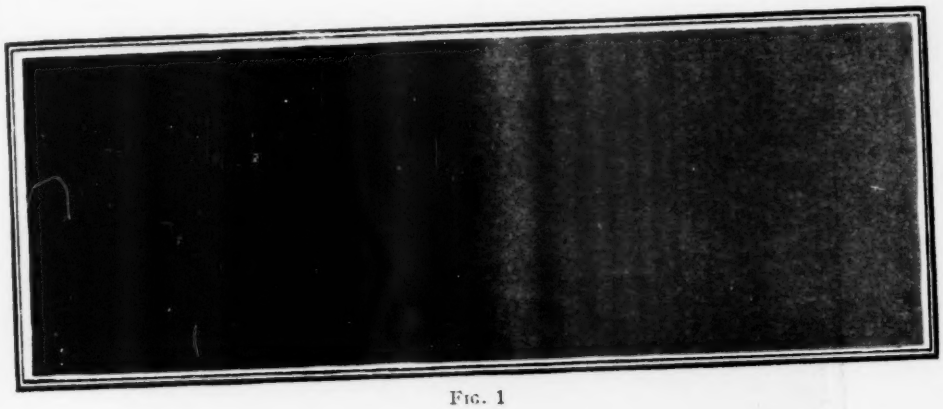

FIG. 1

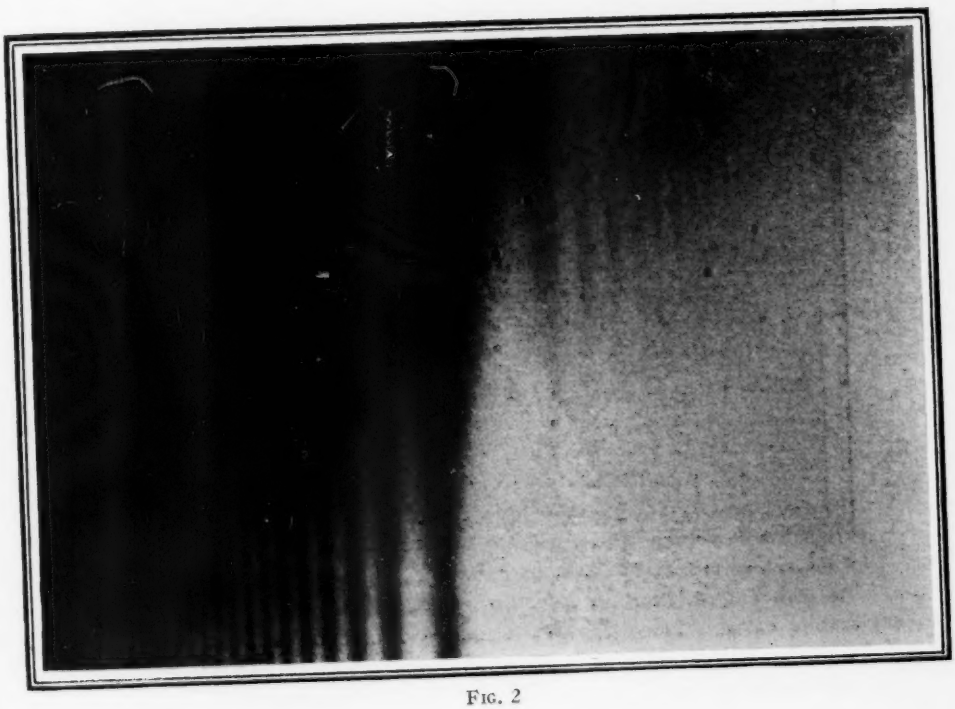

FIG. 2

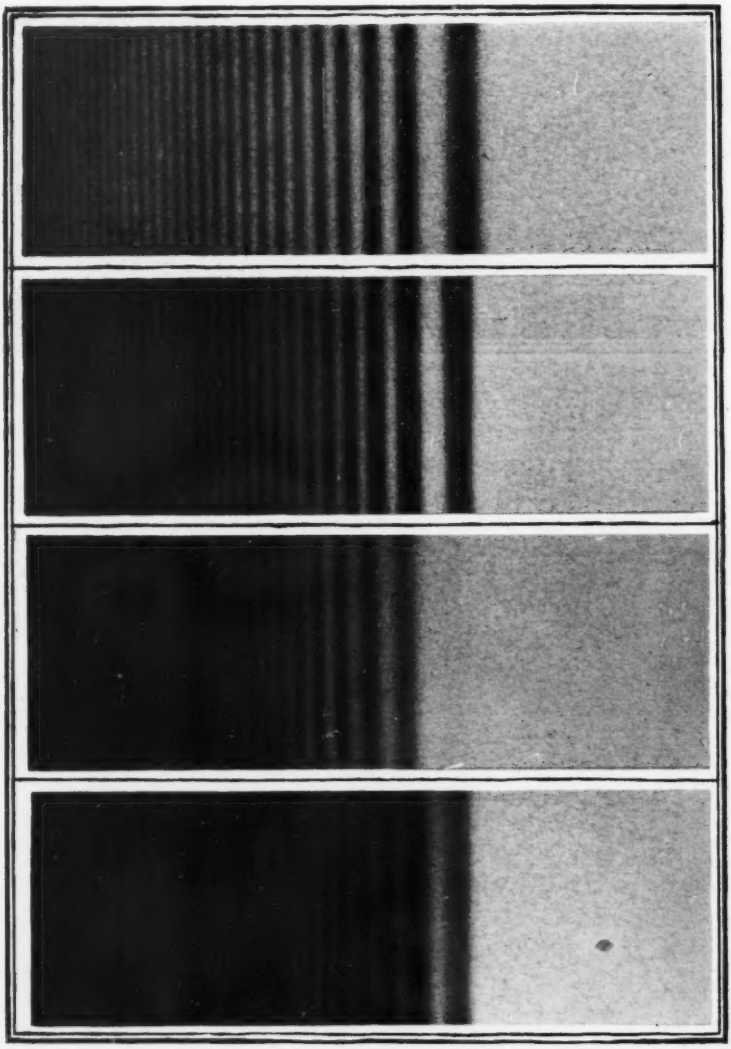

FIG.

STUDIES IN THE CHEMICAL BEHAVIOUR OF SULPHUR COMPOUNDS

Part II. Disulphur Oxide

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Received November 5, 1939

Introductory

While studying the properties of sulphur monoxide, it was noticed in this laboratory, that though sulphur monoxide was a colourless gas, yet the solution obtained by passing it into dry carbon tetrachloride had a deep yellow colour. This yellow solution lost its colour on keeping. Treated with sodium hydroxide immediately on preparation, the solution yielded sulphide, sulphite, and thiosulphate (Experiment *a*), but when the same solution was kept for 24 hours, sodium sulphite was practically the only product obtained in the aqueous layer, on treatment with the alkali (Experiment *b*). This indicated that an unstable oxide of sulphur, hitherto unknown, was present. The ratio of sulphur to oxygen in this compound could be obtained from the analytical values of (*a*) the experiment in which the fresh solution was treated with alkali and (*c*) an experiment in which the oxide was decomposed by mercury and the sulphur dioxide liberated was estimated. The sulphur in the oxide was practically equal to the sulphur corresponding to the soluble compounds of the element, obtained in experiment (*a*), while its oxygen corresponded to that of the sulphur dioxide liberated in (*c*). It was found that the ratio of S to O was approximately 2 : 1 indicating that the oxide had the formula S_2O and was disulphur oxide. An account of the preparation and the properties of the oxide is given in this paper.

Experimental

Sulphur monoxide was obtained by Schenk and his co-workers in a variety of ways (Cordes and Schenk,[2] Schenk and Platz,[16] Schenk and Triebel,[21] Schenk[17]). The method that was found most convenient for purposes of the present investigation was the combustion of sulphur under reduced pressure of oxygen (Schenk[17]). The apparatus employed was essentially the same as described by Schenk. It was however found advantageous

to use a quartz tube for the actual combustion. The oxygen pressure was maintained at 5 to 10 mm. of mercury. In the present investigation, the products of combustion were passed through 40 to 50 c.c. of pure dry carbon tetrachloride contained in a suitable absorption vessel maintained at −12 to −18° C. by a bath of alcohol cooled by carbon dioxide snow. When the gas was passed through the solvent, a deep yellow colour was produced, which as already stated, was found to be due to disulphur oxide. Before the solution could be employed for a study of the properties of the oxide, it was necessary to remove the sulphur dioxide present. To accomplish this, the combustion was stopped, but the current of oxygen continued and the sulphur dioxide pumped off. Investigations with sulphur dioxide solution in carbon tetrachloride had shown that this treatment was adequate for the removal of dissolved sulphur dioxide. It had also been found that it was unnecessary to replace the oxygen by an inert gas like nitrogen for this purpose.

It was found that the freshly obtained solution of disulphur oxide in carbon tetrachloride had a characteristic absorption spectrum (Plate XXI *a*), there being absorption of light from the ultra-violet end upto a wave-length of 4700 Å. The same solution, however, when kept at the laboratory temperature for 2·5 hours gave an absorption spectrum (XXI *b*) which was identical with (XXI *c*) that of a synthetic solution containing sulphur dioxide and sulphur in quantities corresponding to the disulphur oxide originally present, thereby confirming the nature of the decomposition. A constant deviation spectrograph (supplied by Messrs. Adam Hilger, Ltd.) was used for studying the absorption spectrum.

The solution, as obtained in the combustion experiment (after removal of sulphur dioxide), was found to need dilution before the disulphur oxide could be accurately estimated. It was therefore dilutied with a known weight of dry carbon tetrachloride. Three different sets of analytical experiments were then carried out :—

Experiment (a) : *Hydrolysis of freshly prepared oxide with 2 N sodium hydroxide, containing cadmium hydroxide in suspension.*—A dry stoppered bottle containing a thin-walled sealed tube filled with the alkali (and cadmium hydroxide) was weighed and a portion of the carbon tetrachloride solution was then introduced and the sealed tube immediately broken to effect hydrolysis, the contents being shaken for 3 minutes. The bottle was then reweighed and the weight of the carbon tetrachloride solution used, calculated. When hydrolysis was complete, the carbon tetrachloride layer was removed, a separating funnel being used. The aqueous layer was filtered

and the precipitate of cadmium sulphide (and excess cadmium hydroxide) was washed. The filtrate was diluted to 250 c.c. in a measuring flask and aliquots employed for estimation of sulphite and thiosulphate by the method of Kurtenacker and Goldbach.[9] Another aliquot was oxidised with hydrogen peroxide and the sulphate formed, estimated by the method of Pregl. From this sulphate value it could be found if any thionate or sulphate had been formed during hydrolysis. No detectable amounts of thionate or sulphate were found when 2 N alkali was used for hydrolysis as the sulphate obtained corresponded to the sulphite and thiosulphate originally present. The elementary sulphur in solution in carbon tetrachloride was estimated by the method developed in this laboratory and described by B. S. Rao and M. R. A. Rao.[13]

Experiment (b): *Hydrolysis of oxide after keeping for* 24 *hours.*—A weighed quantity of the disulphur oxide solution was kept in a carefully cleaned and dried bottle for a period of 24 hours and the sealed tube of alkali originally placed in it, was broken to effect hydrolysis of the oxide and the products were analysed as in experiment (*a*).

Experiment (c): *Decomposition of disulphur oxide with mercury and estimation of sulphur dioxide liberated.*—A hundred c.c. flask fitted with taps and suitable ground glass connections was weighed along with mercury (5 g.) placed in it, after complete displacement of the air by a stream of pure dry nitrogen. A suitable quantity of the freshly prepared disulphur oxide solution was then introduced into the flask and the flask weighed to obtain the weight of solution used. The sulphur dioxide liberated by the decomposition of the disulphur oxide was removed from the reaction vessel in a stream of dry nitrogen and absorbed in 2 N alkali (holding cadmium hydroxide in suspension). The flask was kept in a bath of boiling water to complete the reaction. The heating was continued till the major part of the carbon tetrachloride had distilled over. To the alkali in the absorption vessel glycerine was then added to inhibit the atmospheric oxidation of sulphite during the subsequent analytical operations. The cadmium hydroxide was filtered off, washed and analysed. No sulphide was found in it. Acetic acid and a known quantity of a standard solution of iodine were added to the filtrate and the excess of iodine left after reaction with the sulphite, was titrated with 0·01 N sodium thiosulphate.

The results obtained can be explained on the basis of the following reactions: When brought in contact with alkali, the major part of the disulphur oxide produces the sulphide and the sulphite of sodium in equimolecular proportions (B. S. Rao[14]).

$$S_2O + H_2O \rightarrow H_2S + SO_2 \text{ Reaction H (Hydrolysis)}$$

and in presence of sodium hydroxide

$$S_2O + 4\,NaOH = Na_2S + Na_2SO_3 + 2\,H_2O$$

Part of the sulphite produced above, reacts with disulphur oxide to give sodium thiosulphate :—

$$2\,Na_2SO_3 + 2\,S_2O + 2\,NaOH = 3\,Na_2S_2O_3 + H_2O \text{ Reaction T (Thionization).}$$

At the same time, the disulphur oxide is decomposed into sulphur and sulphur dioxide :—

$$2\,S_2O = 3\,S + SO_2 \text{ Reaction D (Decomposition)}$$

the sulphur dioxide liberated being absorbed by alkali to give sodium sulphite.

If S_2O corresponding to h atoms of sulphur, participates in reaction H, t atoms in T and d atoms in D, the total quantity of disulphur oxide present in solution will be $h + t + d$, while $h = 2$ sulphide, $t = 2/3$ thiosulphate, and $d = 4/3$ sulphur, formed in the course of the decomposition. It can be shown that the free sulphur should equal thiosulphate + 3 (sulphite-sulphide), all quantities being expressed in gram atoms of sulphur per gram of carbon tetrachloride used as solvent, since sulphide $= h/2$, sulphite $= h/2 - t/2 + d/4$, thiosulphate $= 3\,t/2$, and free sulphur $= 3\,d/4$.

In the following tables, free sulphur calculated on the basis of the above relationship has been termed S (Calculated) while the quantity actually determined by experiment is denoted as S (Found).

The method of calculation of results is indicated with reference to Experiment 1 in Table I. The quantities are expressed in gram atoms of sulphur per gram of carbon tetrachloride in the undiluted soultion of disulphur oxide, and have been multiplied by 10^6. The values of sulphur, h, t, and d have been obtained from the equations indicated above. In Experiment (*c*) the sulphite obtained is 4·62 while the sulphur in carbon tetrachloride solution is 32·85. Only the reaction D takes place in this case and so the S_2O present is four times the sulphite and the sulphur produced by decomposition of the S_2O is three times the sulphite.

$S_2O = 18{\cdot}48$, $S = 13{\cdot}86$.

TABLE I

No. of experiment	1		2		3		4		5		6		7	
	(*a*)	(*b*) Kept 2 hrs.	(*a*)	(*b*) Kept 24 hrs.	(*a*)	(*b*) Kept 6 hrs.	(*a*)	(*b*) Kept 24 hrs.	(*a*)	(*b*) Kept 24 hrs.	(*a*)	(*b*) Kept 24 hrs.	(*a*)	(*b*) Kept 24 hrs.
*Sulphite	4·96	4·06	4·7	3·87	5·36	3·46	1·60	2·22	2·12	3·73	7·47	5·12	6·59	4·87
Sulphide	5·85	0·41	6·3	0·17	5·65	0·45	3·14	0·07	4·72	0·12	10·63	0·54	9·25	0·47
Thiosulphate	6·22	1·63	6·85	1·24	4·47	1·73	4·95	0·43	8·89	0·75	9·54	2·86	9·38	2·52
Free Sulphur (Calcd.) ..	3·55	12·58	2·08	12·34	3·60	10·76	0·33	6·88	1·09	11·58	0·06	16·60	1·40	15·72
h	11·70	0·82	12·60	0·34	11·30	0·90	6·28	0·14	9·44	0·24	21·26	1·08	18·50	0·94
t'	4·15	1·09	4·59	0·73	2·98	1·15	3·30	0·29	5·93	0·50	6·36	1·91	6·25	1·68
d	4·73	16·77	2·77	16·45	4·80	14·35	0·44	9·17	1·45	15·44	0·08	22·13	1·87	20·96
$h + t' + d$	20·58	18·68	19·96	17·62	19·08	16·40	10·02	9·60	16·82	16·18	27·70	25·12	26·62	23·58
S_2O (Expt. c)	18·48	18·48	17·52	17·52	16·40	16·40	9·60	9·60	16·18	16·18	25·12	25·12	23·58	23·58
Activated Sulphur .	2·10	0·20	2·44	0·10	2·68	..	0·42	..	0·64	..	2·58	..	3·04	..
t	2·05	0·89	2·15	0·73	0·30	1·15	2·88	0·29	5·29	0·50	3·78	1·91	3·21	1·68
S in CCl_4 solution (Calcd.)	20·44	31·77	22·58	35·2	30·5	37·9	14·61	21·58	..	..	..	..	33·26	50·62
S in CCl_4 solution (Found)	20·04	31·37	21·87	35·9	29·8	38·5	14·80	21·56	n.d.	n.d.	n.d.	n.d.	32·8	50·21
" Residual " S (Expt. c)	18·99	18·99	22·94	22·94	27·18	27·18	14·7	14·7	..	..	..	..	34·9	34·9
% hydrolysis	63·3	4·4	71·9	1·9	68·9	5·5	65·4	1·5	58·4	1·5	84·6	4·3	78·5	4·0
% thionization	11·1	5·9	12·3	4·2	1·8	7·0	30·0	3·0	32·7	3·1	15·1	7·6	13·6	7·1
% decomposition ..	25·6	90·7	15·8	93·9	29·3	87·5	4·6	95·5	8·9	95·4	0·3	88·1	7·9	88·9

* The quantities of disulphur oxide and of the products of its reaction have been expressed in gram atoms of sulphur per gram of the original solution and have been multiplied by 10^6.

It is obvious that in addition to the sulphur produced by decomposition of S_2O, the carbon tetrachloride holds in solution extra sulphur. This sulphur has been designated " Residual Sulphur " for the sake of convenience. Its value in Experiment 1 is 32·85 less 13·86, *i.e.*, 18·99. This residual sulphur is due to the fact that during the production of disulphur oxide by combustion of sulphur, the oxide formed is continuously decomposing into sulphur and sulphur dioxide and is enriching the sulphur content of the carbon tetrachloride.

It will be noticed that the same solution of disulphur oxide when subjected to the three treatments (*a*), (*b*) and (*c*) described above, indicates varying amounts of disulphur oxide the value in (*a*) being 20·58, in (*b*) 18·68, and in (*c*) 18·48. The difference between (*b*) and (*c*) is not very much above the experimental error and may perhaps be neglected since such differences between S_2O values for (*b*) and (*c*) have been noticed in only one other experiment (Experiment 2). The apparently higher value of S_2O in (*a*) is due to the fact that in carbon tetrachloride solution the disulphur oxide forms a molecular complex with dissolved sulphur as is revealed by molecular weight determinations by the cryoscopic method described later in this paper. When the complex is brought in contact with alkali, the disulphur oxide has the effect of activating a part of the dissolved sulphur and enables it to thionize the sulphite. The thiosulphate content of the solution thus increases and leads to an apparent increase in the amount of disulphur oxide. Thionization in Experiment (*a*) has therefore been denoted by t' which is higher than the true value t. The following mechanism for the activation of part of the dissolved sulphur can be suggested. When the complex between dissolved sulphur and disulphur oxide breaks up on treatment with alkali, it mainly splits up into sulphur and disulphur oxide. Small quantities of S_3O (trisulphur oxide), however, are formed and the extra sulphur present in the molecule thionizes sulphite to yield thiosulphate. It has already been pointed out in Part I of the present studies that S_3Cl_2 a chloride corresponding to S_3O is known to be present in sulphur chloride. The actual S_2O present in all the three cases is 18·48 and the activated sulphur in (*a*) is $(20·58 - 18·48) = 2·1$. This value has to be deducted from t' in (*a*) to give the correct value of t. It has to be pointed out that sulphur dissolved in carbon tetrachloride does not produce detectable quantities of sulphide, sulphite or thiosulphate under the experimental conditions of the hydrolytic treatment of disulphur oxide solutions with alkali.

Confirmation of the view that a part of the dissolved sulphur is activated by disulphur oxide and participates in thionization is afforded by the agreement between the observed and the calculated values of dissolved sulphur

present in the carbon tetrachloride layer in experiments 1 (*a*) and 1 (*b*). In 1 (*a*) the free sulphur in the solvent should be (18·99 + 3·55 − 2·1) where 18·99 is the residual sulphur, 3·55 is the calculated amount of sulphur liberated during treatment with alkali and 2·1 is the activated sulphur. The free sulphur in experiment 1 (*a*) is 20·44 as calculated, and 20·03 as actually found by analysis. The value for free sulphur in 1 (*b*) is 31·77 (Calculated) and 31·37 (Found). The agreement in both the cases is good, considering the experimental difficulties involved in the accurate determination of sulphide, sulphite, thiosulphate and free sulphur in such dilute solutions. It has to be stated that the experimental error in the analytical determinations is of the order of 2 to 4%.

Effect of Duration of Combustion on Yield of Disulphur Oxide

The duration of combustion of sulphur was varied and the corresponding yields of disulphur oxide determined. The results are given in Table II and indicate that the quantity of disulphur oxide produced increased with time. The yields, however, were not reproducible. In two experiments, where the oxygen pressure and the heating of the combustion tube were practically constant and the combustion was carried out for 30 minutes, the S_2O produced corresponded to $17 \cdot 28\ 10^{-6}$ and $19 \cdot 80\ 10^{-6}$ gram atoms of sulphur per gram of solvent. In two similar experiments where the duration of combustion was 120 minutes, the yields were 55·66 and 77·62. The apparent yield per minute of combustion dropped as the duration of combustion increased.

TABLE II

No. of experiment	1 (*a*)	1 (*b*)	2 (*a*)	2 (*b*)	3 (*a*)	3 (*b*)	4 (*a*)	4 (*b*)	5 (*a*)	5 (*b*)	6 (*a*)	6 (*b*)
Duration of Combustion ..	30 minutes		30 minutes		60 minutes		120 minutes		120 minutes		180 minutes	
* Sulphite ..	5·06	4·04	5·29	3·82	11·00	7·83	13·48	11·04	15·81	16·39	20·43	15·58
Sulphide ..	7·72	0·29	7·51	0·17	14·35	0·12	21·27	0·86	26·06	0·39	33·42	1·35
Thiosulphate ..	8·08	2·11	7·10	1·17	11·87	2·08	26·19	6·61	36·98	6·42	42·18	14·14
Sulphur (Calculated) ..	0·10	13·36	0·44	12·12	1·82	25·21	2·82	37·15	6·23	54·42	3·21	56·83
h ..	15·44	0·58	15·02	0·34	28·70	0·24	42·54	1·72	52·12	0·78	66·84	2·70
t' ..	5·39	1·41	4·73	0·78	7·91	1·39	17·46	4·41	24·65	4·28	28·12	9·43
d ..	0·13	17·81	0·59	16·16	2·43	33·61	3·76	49·53	8·31	72·56	4·28	75·77
$h + t' + d$ ..	20·96	19·80	20·34	17·28	39·04	35·24	63·76	55·66	85·08	77·62	99·24	87·90
S_2O ..	19·80	19·80	17·28	17·28	35·24	35·24	55·66	55·66	77·62	77·62	87·90	87·90
S' = Activated Sulphur ..	1·16	Nil	3·06	Nil	3·80	Nil	8·10	Nil	7·46	Nil	11·34	Nil
t ..	4·23	1·41	1·67	0·78	4·11	1·39	9·36	4·41	17·19	4·28	16·78	9·43
S in CCl_4 soln. (Calculated) ..	29·19	..	26·52	..	53·76	..	81·0	..	106·5	..	122·4	..
S in CCl_4 soln. (Found) ..	28·55	43·61	26·95	41·26	54·75	80·34	83·5	123·4	101·1	162·1	130·0	192·8
Residual sulphur	30·25	30·25	29·14	29·14	55·13	55·13	86·25	86·25	107·7	107·7	136·0	136·0
% *h* ..	78·0	2·9	86·9	2·0	81·5	0·7	76·5	3·1	67·1	1·0	76·1	3·1
% *t* ..	21·4	7·1	9·7	4·5	11·6	3·9	16·7	7·9	22·2	5·5	19·1	10·7
% *d* ..	0·6	89·9	3·4	93·5	6·9	95·4	6·8	89·0	10·7	93·5	4·8	86·2
Dilution ..	3·3	..	5·8	..	4·05	..	2·1	..	1·7	..	1·7	..

* The quantities of disulphur oxide and of the products of its reaction have been expressed in gram atoms of sulphur per gram of the original sclution and have been multiplied by 10^6.

TABLE III

Duration of Combustion in minutes	30	60	120	180
Average yield of S_2O (g. atoms of S $\times 10^{-6}$) as S_2O per g. solvent)	18·54	35·24	66·64	87·9
Apparent yield per minute	0·62	0·59	0·56	0·49

The ratio of " Residual Sulphur " to sulphur as disulphur oxide was found to be fairly constant, the values for the five experiments being as follows :—

No. of experiment (Table II) ..	1	2	3	4	5
Ratio Residual S to S as S_2O	1·53	1·69	1·56	1·39	1·55

Mean value 1·55

Rate of Decomposition of Disulphur Oxide

Information about the stability of disulphur oxide in carbon tetrachloride solutions could be obtained from the data presented in Table I. The results (Table IV) showed that no correlation could be established between the rate of decomposition and the concentration of disulphur oxide or of residual sulphur. The stability of the disulphur oxide was found to depend mainly on the condition of the glass surface of the vessel in which the oxide solution was kept.

TABLE IV

Decomposition of Disulphur Oxide (in Carbon Tetrachloride Solution) Stored in Glass Bottles

No. of Expt.	S_2O in 400 g. soln. in g. atoms $\times 10^{-6}$	Duration of storage in hours	% Decomposition	" Residual sulphur"	Ratio S : S_2O
1	18·68	2	90·7	19·0	1·02
2	17·62	24	93·9	22·94	1·30
3	16·40	6	87·5	27·20	1·66
4	9·6	24	95·5	14·7	1·53
5	16·2	24	95·4	n.d.	n.d.
6	25·1	24	88·1	n.d.	n.d.
7	23·6	24	88·9	34·9	1·48

gram of the original solution and have been multiplied by 10^6.

Further studies on the stability of disulphur oxide solutions showed that dissolved sulphur had a noticeable stabilising effect on the oxide. This effect, however, was often masked by the catalytic decomposition taking place at the glass surface. The stabilising effect of dissolved sulphur was analogous to that of the element on the stability of persulphides of hydrogen (Sabatier[15]).

As in the case of persulphides, the dissolved sulphur formed complexes with the disulphur oxide. Decomposition of persulphides of hydrogen is known to be less in glass vessels whose surface has been treated with hydrogen chloride (Butler and Maass[1]). It was found that hydrogen chloride had similar stabilising effect on disulphur oxide.

Effect of Dilution of Disulphur Oxide on the Reaction with Alkali

When disulphur oxide solutions at different dilution were treated with 2 N alkali the relative proportions of the three reactions: H (hydrolysis), T (thionization), D (decomposition) changed as indicated in Table V.

TABLE V

Effect of Dilution of S_2O Solutions on the Reaction with 2 N Alkali (Dilution has been expressed in g. of CCl_4 holding S_2O corresponding to 1 g. atom of S, and has been multiplied by 10^{-5}

Dilution	..	1·7	1·7	2·1	3·1	3·3	3·5	3·7	4·05	5·8
Hydrolysis	..	67·1	76·1	76·5	73·4	78·0	73·7	71·7	81·5	86·9
Thionization	..	22·1	19·1	16·7	21·4	21·4	19·5	26·9	11·6	9·7
Decomposition	..	10·7	4·8	6·8	5·2	0·6	6·8	1·4	6·9	3·4

The effect of dilution was not consistent probably because of the influence of dissolved sulphur (present in varying amounts), but it was noticed that in general, dilution tended to increase hydrolysis and decrease thionization as well as decomposition.

In Part I of the present studies, it was pointed out that the hydrolysis by alkali of sulphur chloride solutions could best be interpreted by assuming that disulphur oxide (or its highly unstable hydrate—the hypothetical thiosulphurous acid) was the primary product of hydrolysis. It is of interest therefore to compare the above results with those obtained in the study of the effect of dilution on the hydrolysis of sulphur chloride (Table VI). It will be noticed that at the same dilution, disulphur oxide and sulphur chloride give approximately the same values for hydrolysis. Thionization, however,

is more in the case of disulphur oxide and decomposition is less. The difference in thionization seems to be due to the fact that in the case of the disulphur oxide solutions we are dealing with a complex between the oxide and dissolved sulphur. This complex presumably is a better thionizing agent than disulphur oxide itself.

Complex formation, resulting in greater stability of the disulphur oxide, may also be responsible for the smaller decomposition noticed with the oxide solutions. An alternative explanation, however, is possible. In consonance with the fact that the lower oxides of sulphur are more stable than their corresponding oxyacids, disulphur oxide is more stable than thiosulphurous acid, which has so far not been isolated though its esters are known and have been studied (Noack,[12] Meuwsen,[10] Hellmuth,[8] Stamm and Wintzer[23]). If thiosulphurous acid itself (and not disulphur oxide) is considered to be the primary product of hydrolysis of sulphur chloride, it is easy to account for the greater decomposition noticed in the case of sulphur chloride hydrolysis.

TABLE VI

Effect of Dilution of Sulphur Chloride on its Reaction with 2 N Alkali (Dilution has been expressed in g. of CCl_4 holding S_2O corresponding to 1 g. atom of S, and has been multiplied by 10^{-5})

Dilution ..	0·7	1·5	3·8	38·0	77·1
Hydrolysis ..	54·2	68·5	75·8	88·6	90·4
Thionization ..	6·2	6·2	9·6	8·1	9·7
Decomposition ..	40·4	28·3	15·9	3·1	0·0

The effect of (*a*) temperature, (*b*) strength and nature of alkali, and (*c*) reagents like formalin and brucine on the hydrolytic decomposition of disulphur oxide have been studied and will be the subject of another paper in this series. In general, the effects are analogous to those noticed in the hydrolytic decomposition of sulphur chloride.

Complex Formation between Disulphur Oxide and Dissolved Sulphur

To throw light on the molecular condition of the disulphur oxide in solution, an attempt was made to determine the molecular weight of the oxide by the cryoscopic method. The crysocopic constant for carbon tetrachloride is particularly high (360° for a g. mole in 100 g. solvent). This enabled reasonably accurate determinations even with highly dilute solutions.

The ordinary Beckmann apparatus was employed, the freezing bath being alcohol to which adequate amounts of carbon dioxide snow were added from time to time, to maintain a temperature of $-24°$ C., the refrigerant being kept in a Dewar bottle. Preliminary experiments were carried out with dilute solutions of sulphur in carbon tetrachloride, the sulphur concentration being of the order of 20×10^{-6} g. atom per g. of solvent. For the atomicity of the sulphur molecule the values obtained were 8·06 and 8·18 (mean value 8·12). A solution of disulphur oxide was prepared and divided into two portions. One sample was treated with 2 N alkali to determine the S_2O and the residual sulphur present. The other sample was used for the cryoscopic work. The freezing point depression observed was of the order of 0·5°. After determination of the freezing point, the solution was treated with alkali to determine S_2O still left in solution. It was noticed that on an average, 3 to 4 % of the S_2O originally present had decomposed. Three determinations were carried out. The results are given in Table VII.

TABLE VII

Cryoscopic Work on Disulphur Oxide Solutions in Carbon Tetrachloride

No. of Experiment	1	2	3
Fr. pt. lowering	0·500°	0·785°	0·527°
Moles of complex $\times 10^{-6}$ per g. of soln.	13·89	21·81	14·64
$S_2O \times 10^{-6}$	72·9	103·8	68·76
"Residual Sulphur"	99·9	147·7	70·28
$S_2O + S$	172·8	251·5	139·04
S atoms per mol. of complex	12·44	11·53	9·49
S_2O per mol. of complex	5·25	4·76	4·70
Sulphur per mol. of complex	7·19	6·77	4·78
Molecules of S_2O in union with mole of sulphur (S_8)	2·92	2·81	3·90

The results indicated that the disulphur oxide in solution formed a complex with the dissolved sulphur. The number of moles of S_2O associated with a mole of sulphur varied with the concentration. It is of interest to note that Schenk[18] found that when sulphur monoxide was condensed by refrigeration, the sulphur residues, after removal of the monoxide, contained oxygen in combination. He suggested that the monoxide gave off sulphur dioxide and formed complexes between the sulphur liberated and the residual monoxide.

In the opinion of the present author, there is definite formation of disulphur oxide when sulphur monoxide is passed into cold carbon tetrachloride and not mere complex formation between sulphur and sulphur monoxide. He also considers it very probable that disulphur oxide is produced when sulphur monoxide is condensed by refrigeration as in Schenk's experiments. The production of sodium sulphide when the carbon tetrachloride solution is treated with alkali cannot easily be accounted for, excepting on the basis of formation of disulphur oxide. The quantitative study presented in this paper, of the reaction between the solution of the products of combustion of sulphur in oxygen at low pressure and alkali has shown that disulphur oxide and sulphur are the only constituents in solution after the removal of sulphur dioxide.

Decomposition of Sulphur Monoxide to Disulphur Oxide

From their investigations on the free energy of sulphur monoxide, Montgomery and Kassel[11] have concluded that the gas is moderately stable with respect to sulphur and sulphur dioxide at flame temperatures but that it is unstable below 1000° K. Cordes and Schenk[4] have claimed that sulphur monoxide can be stored for two days in a quartz tube without complete decomposition. The stability of sulphur monoxide has been further considered by them in a later paper.[5] It is of interest to note that more recently Cordes[6] has thrown doubt on the very existence of sulphur monoxide and has stated that the absorption band (which has been of great value in studying the gas) merely indicates the existence of metastable S_2. Schenk[19] on the other hand considers that a reactive oxygen compound of sulphur is responsible for the phenomena observed. By postulating the production of disulphur oxide (containing the S = S linkage) as caused by the decomposition of sulphur monoxide primarily formed, the divergent views expressed by the original discoverers of sulphur monoxide may be bridged. The disulphuroxide seems to be formed by the following reaction between sulphur monoxide and the disulphur dioxide:—

$$SO + S_2O_2 = S_2O + SO_2$$

Disulphur dioxide, it may be pointed out, is readily formed by the polymerisation of the monoxide. From their investigations on sulphur monoxide, Schenk and Platz[20] have concluded that nearly two-thirds of the monoxide is associated as disulphur dioxide in the vapour state. Cordes and Schenk[3] also assumed polymerisation of sulphur monoxide to account for their observation that on condensation, sulphur monoxide cannot again be completely vapourised.

The sulphur monoxide preparations obtained by Schenk and Platz[20] gave with 5 N alkali at 0° C. sulphite, sulphide and thiosulphate but no sulphate, hyposulphite (hydrosulphite) or polythionates. The formation of sulphide, without the concomitant production of sulphate is significant as it indicates the presence of disulphur oxide. For, sulphide formation from disulphur dioxide or sulphur monoxide is possible, only if sulphate is simultaneously formed :—

$$S_2O_2 + 2\,H_2O = H_2S + H_2SO_4$$

Hydrolysis of the above type does not take place with alkali and disulphur dioxide. It only takes place in strongly acid medium (Foerster and Umbach[7]). In their earliest communications, Cordes and Schenk[2,3] claimed the production of sodium sulphoxylate and sodium hyposulphite when their sulphur monoxide preparations were brought in contact with alkali but in a subsequent paper, Schenk and Platz[20] state that they have not obtained any hyposulphite or sulphoxylate. Production of either of these salts can be looked upon as chemical evidence of the presence of sulphur monoxide. The present author has repeatedly tried the action of alkali on sulphur monoxide preparations but has failed to obtain any evidence of the formation of sulphoxylate or hyposulphite. Of particular significance is the fact that Scholder and Denk[22] failed to obtain sodium sulphoxylate in aqueous solution. The reaction employed by them yielded only sodium thiosulphate. It is therefore to be concluded that there is scarcely any irreproachable chemical evidence of the existence of the monoxide in the liquid obtained by the refrigeration of the products of combustion of sulphur (in oxygen at low pressure) or in the cold carbon tetrachloride into which the combustion products are passed. The chemical evidence on the other hand supports the existence of disulphur oxide, though it does not exclude the probable presence of disulphur dioxide, which yields thiosulphate with alkali.

Summary

(1) When the products of combustion of sulphur in oxygen under highly reduced pressure are passed into cold carbon tetrachloride, disulphur oxide is produced.

(2) It is suggested that the primary product of combustion is probably the highly unstable sulphur monoxide. Part of the monoxide polymerises to yield disulphur dioxide and the reaction between the polymer and the monoxide produces disulphur oxide and sulphur dioxide :—

$$S_2O_2 + SO = S_2O + SO_2$$

(3) Disulphur oxide (in carbon tetrachloride solutions) is unstable and decomposes into sulphur and sulphur dioxide :—

$$2\,S_2O = 3\,S + SO_2$$

(4) As revealed by cryoscopic studies, disulphur oxide exists in carbon tetrachloride solutions, in the form of a complex with the dissolved sulphur present—a molecule of sulphur (S_8) uniting with 3 or 4 molecules of disulphur oxide.

(5) The complex in carbon tetrachloride solution gives an absorption band which extends from the ultra-violet end to a wave-length of 4700 Å.

(6) The dissolved sulphur (by forming a complex) renders the disulphur oxide more stable.

(7) The decomposition of dissolved disulphur oxide is greatly influenced by the nature of the glass surface of the containing vessel. Hydrogen chloride (as with persulphide solutions) retards the decomposition at the glass surface.

(8) When dilute solutions of disulphur oxide are treated with aqueous solutions (2 N) of sodium hydroxide, the major part of the oxide is hydrolysed to sodium sulphide and sodium sulphite which are formed in equimolecular proportions.

(9) The disulphur oxide thionizes part of the sulphite (formed by hydrolysis) to yield sodium thiosulphate.

(10) Owing to complex formation, a part of the sulphur present in carbon tetrachloride solution is activated by the disulphur oxide and rendered capable of converting sulphite to thoisulphate. The activation is probably due to the formation of small quantities of trisulphur oxide (S_3O) (corresponding to the chloride S_3Cl_2) when the complex breaks up in reacting with alkali.

(11) The effect of dilution on the hydrolysis of disulphur oxide is compared with that noticed in the case of sulphur chloride hydrolysis by 2 N alkali.

The author gratefully acknowledges the valuable assistance of his colleague Mr. M. R. Aswathnarayana Rao, in carrying out part of the analytical work described in this paper.

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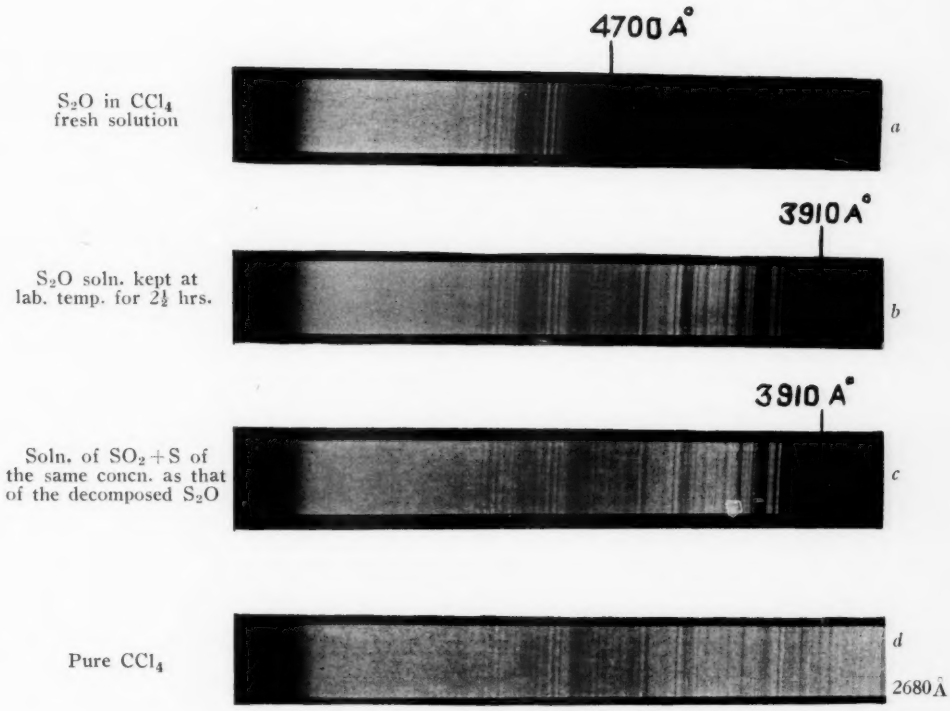
1881-39—Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao Superintendent, and Published by The Indian Academy of Sciences, Bangalore


4700 A°
S_2O in CCl_4 fresh solution
a
3910 A°
S_2O soln. kept at lab. temp. for 2½ hrs.
b
3910 A°
Soln. of $SO_2 + S$ of the same concn. as that of the decomposed S_2O
c
Pure CCl_4
d
2680 Å

Errata

Vol. X, No. 5, November 1939—

On page 367, Table XII, under *c*, against Li 6708 *read* 173·5 *for* 173.

On page 374, Table XXVI, under *c*, against Li 6708 *read* 160·5 *for* 160·7.

Page 409, line 12, *read* "with the assumption" *instead of* "with the D. N. Moghe assumption".

Page 416, Equation (71), *read* $ar_b^2 - Tr_b + 2\alpha T^2 + 2\beta T = 0$ *instead of* $s\pi_b^2 - Tr_b + 2\alpha T^2 + 2\beta T = 0$.

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